REMARKS

Claims 1-16 are pending in the above-identified application with claims 5-9 and 11-12 being withdrawn from consideration due to an earlier Restriction Requirement, and remaining claims 1-4, 10 and 13-16 standing ready for further action on the merits.

Claim Rejections Under 35 USC § 102/103

Claims 1-4, 10 and 13-16 are rejected under 35 USC § 102(b) as anticipated by or, in the alternative, under 35 USC § 103(a) as obvious over Helmer-Metzmann et al. (US 5,741,408). Reconsideration and withdrawal of these alternative rejections over the Helmer-Metzmann et al. '408 reference are respectfully requested based upon the following considerations.

The Examiner maintains the outstanding rejection as set forth in the previous Office Action. Additionally, the Examiner asserts that the limitation "wherein the one or more blocks having substantially no sulfonic acid group is/are introduced from precursors having a weight-average molecular weight of not less than 2000" is considered to be a product-by-process limitation insofar as the "blocks" are *introduced* from precursors, i.e., starting materials. The Examiner also asserts that the limitation is absent of any structural features and as such, is not given

patentable weight and does not give breadth or scope to the product claim.

In response to the Examiner's assertions, the Applicants point out that the molecular weight of a precursor introduced into the block polymer is typically and usually maintained before and after the block polymer is produced, that is, the molecular weight of the segment in the block polymer derived from the precursor is the same as, or more than, that of the precursor since cleavage of the carbon chain seldom occurs.

Therefore, while the Examiner may wish to assert that the limitation (of the molecular weight of precursor) is absent of any structural feature, Applicants do *not* agree with the Examiner's position and ask for reconsideration of the same. In this respect, Applicants again submit that based on the limitations recited in the claims, made by the previous amendment, the present claims are clearly distinguishable from Helmer-Metzmann et al. (US 5,741,408).

In support of the above contention, the Examiner's attention is directed to the enclosed technical reference "COMPREHENSIVE POLYMER SCIENCE, The Synthesis, Characterization, Reactions & Applications of Polymers, Sir Geoffrey Allen Editor, Volume 6, Polymer Reactions, Chapter 11, Heterochain Block Copolymers, pages 369-401, Pergaman Press pcl (1989)".

According to the teachings of the enclosed Comprehensive Polymer Science reference, for example, at sections 11.1.2.3 (see page 373), 11.1.2.4 (see page 375) and 11.2.7 (see page 394), it is shown that starting oligomer, that is, precursor, incorporated into produced block copolymer maintains its structure.

Based on the above considerations, it is clear that the present claims, while being formally defined by the way of product-by-process according to the Examiner, are also clearly defined by way of block copolymer structure. In this respect, Helmer-Metzmann et al. '408 does not disclose, teach or otherwise render obvious the instantly recited structural limitation of "one or more blocks having substantially no sulfonic acid group … introduced from precursors having a weight-average molecular weight of not less than 2000".

Accordingly, based upon the above considerations, it is clear that the cited Helmer-Metzmann et al. '408 reference is incapable of either anticipating or rendering obvious Applicants' invention as instantly claimed. In this respect, the reference does not teach each of the elements recited in the pending claims, which elements must be given patentable weight by the Examiner, and at the same time provides no teachings, or other motivations which would allow one of ordinary skill in the art to arrive at the

4

present invention as claimed. As such, the outstanding rejections under 35 USC § 102 and 35 USC § 103 are not sustainable.

Earlier Filed IDS's

Applicants appreciate the Examiner's courtesy in supplying copies of the earlier filed PTO-1449 forms.

At page 4 of the outstanding Office Action, the Examiner comments on earlier filed Information Disclosure Statements. The Examiner comments that certain references earlier submitted were not considered. Accordingly, enclosed herewith is a new 1449 form having listed thereon certain references, which were not previously considered by the Examiner, even though included with Applicants earlier IDS paper submissions. The Examiner is respectfully requested to review each of the accompanying documents, including the English translations thereof provided and/or the English language foreign search report from the European Patent Office (also enclosed) indicating the relevancy of the same. Thereafter, the Examiner is respectfully requested to provide an initialed copy of the attached 1449 form to the Applicants.

For completeness, it is also noted that earlier submitted references JP 4-363121 and JP 5-15743 noted at item "a." of page 4 of the Office Action correspond to US 5,300,228, which has already been considered by the Examiner.
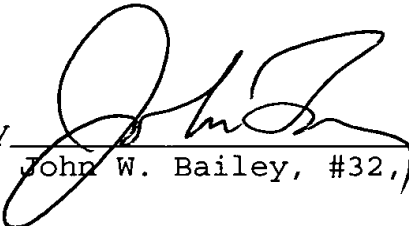
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CONCLUSION

Based upon the remarks presented herein, the Examiner is respectfully requested to issue a Notice of Allowance clearly indicating that each of the pending claims under consideration (claims 1-4, 10 and 13-16) are allowed and patentable under the provisions of Title 35 of the United States Code.

Should there be any outstanding matters that need to be resolved in the present application, the Examiner is respectfully requested to contact John W. Bailey (Reg. No. 32,881) at the telephone number below, to conduct an interview in an effort to expedite prosecution in connection with the present application.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. §§ 1.16 or 1.17; particularly, extension of time fees.

Respectfully submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

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JWB/enm
2185-0497P

6

Attachments: PTO-1449 Form & References;
Comprehensive Polymer Science, The Synthesis, Characterization, Reactions & Applications of Polymers.

Form PTO-1449	ATTY. DOCKET NO. 2185-0497P	APPLICATION NO. 09/742,115
INFORMATION DISCLOSURE CITATION **IN AN APPLICATION** (Use several sheets if necessary)	APPLICANT TERAHARA et al.	
	FILING DATE December 22, 2000	GROUP 1745

U.S. PATENT DOCUMENTS

EXAMINER INITIAL	DOCUMENT NUMBER		Kind	DATE	NAME	CLASS	SUB CLASS	FILING DATE IF APPROPRIATE
	US							
	US							
	US							
	US							
	US							
	US							
	US							
	US							
	US							
	US		.					

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FOREIGN PATENT DOCUMENTS

	Office	DOCUMENT NUMBER	Kind	DATE	COUNTRY	CLASS	SUB CLASS	TRANSLATION YES	TRANSLATION NO
		EP0575801	A1	1993-12-29	EPO				X
		EP0932213	A1	1999-07-28	EPO				
		WO96/29360	A1	1996-09-26	PCT			Abs	
		EP0008894	A1	1980-03-19	EPO				

OTHER DOCUMENTS (Include Name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.) date, page(s), volume-issue number(s), publisher, city and/or country where published.

EXAMINER	DATE CONSIDERED

EXAMINER: Initial if citation considered, whether or not citation is in conformance with M.P.E.P. 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

PTO-1449

JWB/enm

Henkel, Feiler, Hänzel
Möhlstrasse 37
81675 München
ALLEMAGNE

EINGEGANGEN
17. Juni 2003
Henkel, Feiler & Hänzel

Datum/Date
13. 06. 03

Zeichen/Rel./Réf.	Anmeldung Nr./Application No./Demande n°./Patent Nr./Patent No./Brevet n°.
11104/CH/bm	00128267.2 – –

Anmelder/Applicant/Demandeur/Patentinhaber/Proprietor/Titulaire
Sumitomo Chemical Company, Limited

COMMUNICATION

The European Patent Office herewith transmits

[X] the European search report

[ ] the declaration under Rule 45 EPC

[ ] the partial European search report under Rule 45 EPC

[ ] the supplementary European search report concerning the international application under Article 157(2) EPC relating to the above-mentioned European patent application. Copies of the documents cited in the search report are enclosed.

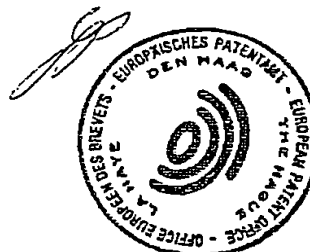The following specifications given by the applicant have been approved by the Search Division :

[X] Abstract   [X] Title   [ ] Figure

[ ] The abstract was modified by the Search Division and the definitive text is attached to this communication.

[ ] The following figure will be published with the abstract, since the Search Division considers that it better characterises the invention than the one indicated by the applicant.

Figure:

[X] Additional copy(copies) of the documents cited in the European search report.

REFUND OF THE SEARCH FEE

If applicable under Article 10 Rules relating to fees, a separate communication from the Receiving Section on the refund of the search fee will be sent later.

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

European Patent
Office

LACK OF UNITY OF INVENTION
SHEET B

Application Number

EP 00 12 8267

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-4,
   10-13 (insofar as they concern the blocks composed of the units represented by the general formula '1!)

   Product claims 1-4 and 10 disclose a polymer electrolyte containing a block copolymer comprising one or more blocks having sulphonic acid groups (units represented by the general formula 1) and one or more blocks having substantially no sulphonic acid groups, wherein at least one block among all the blocks is a block having aromatic rings in the main chain.
   Method claims 11 and 12 disclose a method of producing said polymer electrolyte and product claim 13 discloses a fuel cell using said polymer electrolyte.

2. Claims: 5,
   11-13 (insofar as they concern the blocks composed of the units represented by the general formula '2!)

   Product claim 5 discloses a polymer electrolyte containing a block copolymer comprising one or more blocks having sulphonic acid groups (units represented by the general formula 2) and one or more blocks having substantially no sulphonic acid groups, wherein at least one block among all the blocks is a block having aromatic rings in the main chain.
   Method claims 11 and 12 disclose a method of producing said polymer electrolyte and product claim 13 discloses a fuel cell using said polymer electrolyte.

3. Claims: 6,7,
   11-13 (insofar as they concern the blocks composed of an epoxy resin)

   Product claims 6 and 7 disclose a polymer electrolyte containing a block copolymer comprising one or more blocks having sulphonic acid groups (epoxy resin) and one or more blocks having substantially no sulphonic acid groups, wherein at least one block among all the blocks is a block having aromatic rings in the main chain.
   Method claims 11 and 12 disclose a method of producing said polymer electrolyte and product claim 13 discloses a fuel cell using said polymer electrolyte.

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

4. Claims: 8.9,
   11-13 (insofar as they concern the blocks composed of the units represented by the general formula '4!)

Product claims 8 and 9 disclose a polymer electrolyte containing a block copolymer comprising one or more blocks having sulphonic acid groups and one or more blocks having substantially no sulphonic acid groups (units represented by the general formula 4), wherein at least one block among all the blocks is a block having aromatic rings in the main chain.
Method claims 11 and 12 disclose a method of producing said polymer electrolyte and product claim 13 discloses a fuel cell using said polymer electrolyte.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 438 082 A (RITTER HELMUT ET AL) 1 August 1995 (1995-08-01) * the whole document *	1-4, 10-13	H01M8/10 H01B1/12 C08F8/36
X	US 5 561 202 A (RITTER HELMUT ET AL) 1 October 1996 (1996-10-01) * the whole document *	1-4, 10-13	
X	US 5 741 408 A (RITTER HELMUT ET AL) 21 April 1998 (1998-04-21) * the whole document *	1-4, 10-13	
X	US 5 834 566 A (HELMER-METZMANN FREDDY ET AL) 10 November 1998 (1998-11-10) * the whole document *	1-4, 10-13	
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 06, 30 April 1998 (1998-04-30) -& JP 10 045913 A (SUMITOMO CHEM CO LTD), 17 February 1998 (1998-02-17) * the whole document *	1-4, 10-13	
A	US 5 429 759 A (ANDRIEU XAVIER ET AL) 4 July 1995 (1995-07-04) *column 2, lines 5-9 and lines 65-68; column 3, line 30; claims 1,3,4*	5-7, 11-13	
A	US 3 751 376 A (QUENTIN J) 7 August 1973 (1973-08-07) *column 1, lines 20-25 and line 57; column 3, lines 15-35*	6,7, 11-13	
X	WO 96 29360 A (CLAUSS JOACHIM ;DECKERS GREGOR (DE); HOECHST AG (DE); WITTELER HEL) 26 September 1996 (1996-09-26) *pages 1, 3, 4, 5, 8, 15-19; claims 1, 5*	8,9, 11-13	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

H01M
H01B
C08L
C08G
C08F

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	2 June 2003	Boussard, N

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 575 807 A (HOECHST AG) 29 December 1993 (1993-12-29) *page 2, lines 50-55; page 3, lines 50-52; page 4, lines 10-35*	8,9, 11-13	
X	EP 0 932 213 A (SUMITOMO CHEMICAL CO) 28 July 1999 (1999-07-28) *page 3, lines 1-52; page 4, lines 1-50*	8,9, 11-13	
A	EP 0 008 894 A (ICI PLC) 19 March 1980 (1980-03-19) * the whole document *	8,9, 11-13	

TECHNICAL FIELDS
SEARCHED (Int.Cl.7)

9

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	2 June 2003	Boussard, N

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 00 12 8267

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02-06-2003

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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EPO FORM P0459

(12) **EUROPÄISCHE PATENTANMELDUNG**

(54) Sulphonierte Polyetherketonen.

(57) Es werden Polymerelektrolyte beschrieben, die aus einem sulfonierten aromatischen Polyetherketon Z. B. der allgemeinen Formel II, bestehen

wobei
$a = 0.2 - 1$,
$c = 0 - 0.8$ bedeutet und
$a + c = 1$ ist.
Zu ihrer Herstellung wird ein aromatisches Polyetherketon in Schwefelsäure von 94-97 Gew.-% gelöst und die Lösung mit einem sulfonierenden Agens, z.B. Oleum, versetzt, bis die Schwefelsäure-Konzentration 98 - 99.9 Gew.-% beträgt.

Die Erfindung betrifft Polymerelektrolyte, die aus einem sulfonierten aromatischen Polyetherketon bestehen, sowie Verfahren zur Herstellung dieser Polymerelektrolyte.

Sulfonierte Polyetherketone stellen Kationen-Ionenaustauscher dar. Sie sind nützlich als Membranmaterialien, z.B. zur Ultrafiltration, zur Entsalzung und Entfernung von Mikroorganismen, da sie in vielen Fällen auch in Gegenwart von Wasser mechanisch beständig sind.

Die Herstellung von sulfonierten Polyaryletherketonen wird beschrieben in EP-A-08895 und EP-A-041780. Gemäß EP-A-8895 wird das zu sulfonierende Polymer bei Raumtemperatur in Schwefelsäure von 98 Gew.-% suspendiert. Der Löseprozeß und die Sulfonierung laufen gleichzeitig ab, wobei allmählich eine sehr viskose Lösung erhalten wird. Diese Lösung wird entweder sich selbst überlassen oder bei gleicher Temperatur mit Schwefelsäure gleicher Konzentration verdünnt. Die Reaktion verläuft sehr langsam. Nach Angaben der Autoren waren erst nach 10 Wochen ca. 90 % der sulfonierbaren Phenylen-Einheiten sulfoniert. In den eingesetzten Etherketonen betrug das Zahlenverhältnis von Etherbrücken zu CO-Brücken etwa 2:1.

Nach dem Verfahren gemäß EP-A-41780 werden bei erhöhter Temperatur aromatische Polyetherketone, die Copolymere darstellen, sulfoniert. Nur ein Teil der Monomereinheiten (A) ist der Sulfonierung zugänglich, während Monomereinheiten (B) nicht sulfoniert werden. Durch das Verhältnis A/B läßt sich so der Sulfonierungsgrad steuern. Jedoch bleiben auch hier die Reaktionsbedingungen während des Löseprozesses und danach unverändert.

Entsprechende Homopolymere (A) würden unter den angegebenen Bedingungen zu hoch sulfoniert sein und damit zu wasserlöslichen Verbindungen führen. Da hier die Sulfonierung bereits während des Auflöseprozesses des Polymeren stattfindet, ist es schwierig, den Sulfonierungsgrad zu kontrollieren und niedrig sulfonierte Produkte zu erhalten.
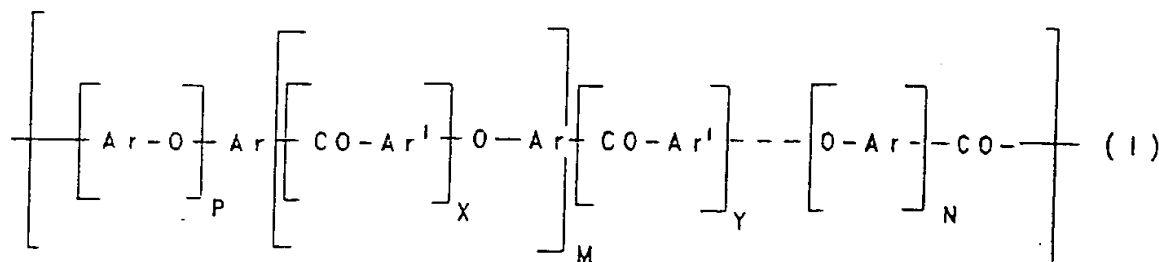
Da bei den beschriebenen Verfahren die Reaktionsbedingungen sich während der Reaktionszeit praktisch nicht verändern, wird ein erheblicher Teil der Sulfonsäuregruppen bereits während des Löseprozesses eingeführt. Der Nachteil dieser Sulfonierungsverfahren besteht darin, daß unter milden Bedingungen die Reaktion sehr langsam verläuft und unter drastischen Bedingungen sulfonierte Produkte nur schlecht rein zu erhalten sind. Die Verwendung von konzentrierter Schwefelsäure als Sulfonierungsreagenz und als Lösungsmittel hat den Nachteil, daß während der Behandlung der Polyetherketone Zersetzungsreaktionen und/oder Vernetzungsreaktionen eintreten (vgl. EP 08 895).

Eine Kontrolle des Sulfonierungsgrades der Polyetherketone während des Prozesses ist sehr wichtig. Die Isolierung der Produkte aus dem wäßrigen Aufarbeitungsmilieu wird mit zunehmendem Sulfonierungsgrad immer schwieriger. Je nach Polymerstruktur bilden die sulfonierten Produkte ab einem bestimmten Sulfonierungsgrad in Wasser hochgequollene Gele oder emulsionsartige Niederschläge, die z.B. zur Herstellung von Membranen ungeeignet sind.

Marvel et al. berichten (Journal of Polymer Science, Polymer Chem. Edition, vol. 23, 2205-2223, (1985)) über die Sulfonierung von Polyetherketonen unterschiedlicher Ether/Keton-Sequenzen unter Verwendung von Chlorsulfonsäure oder einem SO_3/Triethylphosphat-Komplex. Mit dem letztgenannten System wurde dabei ein hoher Grad an Vernetzung sowie Zersetzung der Polymerhauptkette beobachtet. Dagegen war die Chlorsulfonsäure-Route erfolgreicher, obwohl auch hier als wesentliche Nebenreaktion die Zersetzung der Polymerhauptkette eintrat. In Untersuchungen von Bishop et. al., Macromolecules, 18, 86-93 (1985), wurden bei der Sulfonierung von Polyetherketonen mit Chlorsulfonsäure ebenfalls Vernetzungsreaktionen gefunden.

Es bestand daher die Aufgabe, ein Verfahren bereitzustellen, das eine schnelle und schonende Sulfonierung von aromatischen Polyetherketonen gestattet und ferner die Aufgabe, mittels dieses Verfahren neue sulfonierte Polyetherketone zu gewinnen.

Es wurde nunmehr ein Verfahren gefunden, nach dem sich aromatische Polyetherketone der allgemeinen Formel I

$$\left[\left[Ar-O\right]_P Ar\left[\left[CO-Ar'\right]_X O-Ar\left[CO-Ar'\right]_Y\right]_M --- \left[O-Ar\right]_N CO-\right] \quad (I)$$

wobei

Ar   einen Phenylenring mit para- und/oder meta-Bindungen,

Ar'-   einen Phenylen-, Naphthylen-, Biphenylylen-, Anthrylen- oder eine andere zweiwertige aromatische Einheit,

X, M und N   unabhängig voneinander Null oder 1,

Y   Null, 1, 2 oder 3,

p   1, 2, 3 oder 4,

bedeuten, sulfonieren lassen. Das Verfahren ist dadurch gekennzeichnet, daß man das aromatische Polyetherketon in Schwefelsäure von 94 bis 97 Gew.-% löst, man die erhaltene Lösung mit einem sulfonierenden Agens versetzt, bis die Schwefelsäurekonzentration 98 bis 99,5 Gew.-% beträgt und man den Reaktionsansatz aufarbeitet, sobald der gewünschte Sulfonierungsgrad erreicht ist.

Die in Formel I angegebenen aromatischen Polyetherketone sind leicht zugänglich. Die für die Sulfonierung eingesetzten polymeren aromatischen Etherketone lassen sich prinzipiell durch eine elektrophile Polykondensation nach Friedel-Crafts aufbauen, wobei ein entsprechendes aromatisches Bissäuredihalogenid mit einem aromatischen Ether umgesetzt wird. Diese Möglichkeit ist z.B. in US-3 065 205, GB-971 227, US-3 441 538, GB-1 387 303, WO 84-03 891 und in dem Aufsatz von Iwakura, Y., Uno, K. und Tahiguchi, T.J., Polym. Sci., Pat. A-1, 6, 3345 (1968), dargestellt.

Daneben kann man die Etherketone durch nucleophile aromatische Substitution gewinnen. Hierzu wird ein entsprechendes aromatisches Bisdiol mit einem aromatischen Bishalogenketon umgesetzt, wie es z.B. in:

R.A., Clendinning, A.G. Farnham, W.F. Hall, R.N. Johnson and C.N. Merriam, J. Polym. Sci. A1, 5, 2375, (1967), GB-1 177 183, GB-1 141 421, EP-0 001 879, US 4 108 837, US 4 175 175, T.E. Attwood, A.B. Newton, J.B. Rose, Br. Polym. Journ., 4, 391, (1972); T.E. Attwood, P.C. Dawson, J.L. Freemann, L.R.J. Hoy, J.B. Rose, P.A. Staniland, Polymer, 22, 1096, (1981) beschrieben wird.

Das Polymere mit p = 1, X = 0, M = 1, Y = 0, N = 0, ist unter der Bezeichnung ®Victrex im Handel verfügbar. Polymere, in denen N = 1 oder Y = 3 oder p = 4 oder X = 1 beträgt, lassen sich vorzugsweise nach einem nucleophilen Verfahren herstellen.

Vorzugsweise werden die aromatischen Polyetherketone in Schwefelsäure unter schonenden Bedingungen gelöst, d.h. unter Bedingungen, bei denen eine Sulfonierung weitgehend unterdrückt wird, bzw. es noch nicht zu einer Sulfonierung kommt. Angaben über den Sulfonierungsgrad bei der Sulfonierung des Homopolymeren der allgemeinen Formel IV bei unterschiedlichen Lösebedingungen finden sich in X. Jin, M.T. Bishop, T.S. Ellis und F.E. Karasz, British Polymer Journal, Vol. 17, (1985), p. 4-10.

Nach Angaben der Autoren wurde in Schwefelsäure von 94 % nach 3,75 Stunden bei 25°C ein Sulfonierungsgrad von 4 % gefunden. Nach eigenen Untersuchungen bei 25°C wird in Schwefelsäure von 95 % nach 30 Stunden ein Sulfonierungsgrad von 25 % und in Schwefelsäure von 96,2 % nach 24 Stunden ein Sulfonierungsgrad von 32 % beobachtet. Bevorzugt sind für diese Polymere Lösebedingungen, die zu einem Sulfonierungsgrad von maximal 35 % führen.

Für das Homopolymer der allgemeinen Formel VI wird nach eigenen Untersuchungen bei 25°C in Schwefelsäure von 95 % oder 96,2 % nach 5 Stunden ein Sulfonierungsgrad von 14 % beobachtet. Die Konzentration der Schwefelsäure ist in diesem Fall also von geringerer Bedeutung. Bevorzugt sind für dieses Polymer Lösebedingungen, die zu einem Sulfonierungsgrad von maximal 15 % führen.
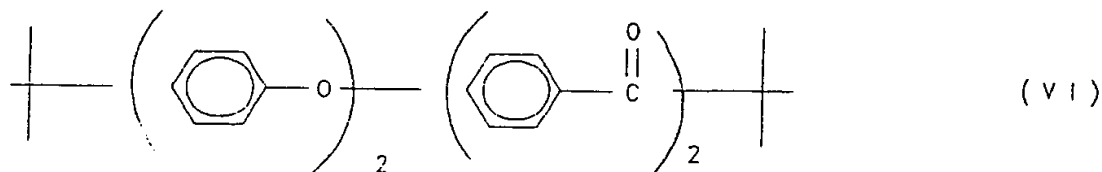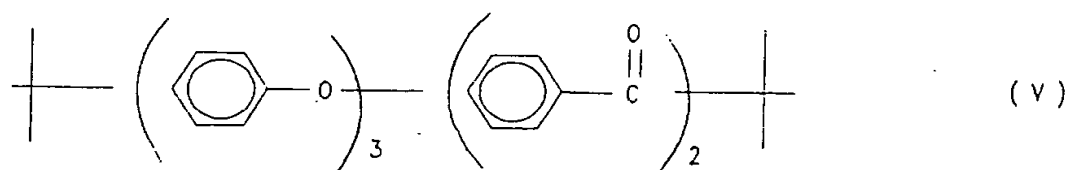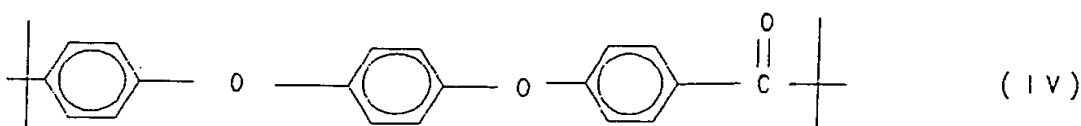
Vorzugsweise bestehen sämtliche zweiwertige aromatische Reste Ar- des zu sulfonierenden Polymers aus Phenylen, vorzugsweise aus 1,4-Phenylen. Als sulfonierendes Agenz, das zur Erhöhung der Schwefelsäure-Konzentration und zur Sulfonierung dient, werden vorzugsweise rauchende Schwefelsäure, Chlorsulfonsäure und Schwefeltrioxid eingesetzt.

Vorzugsweise beträgt die Konzentration der zum Auflösen verwendeten Schwefelsäure 96 bis 96,5 %. Die Lösetemperatur ist abhängig von dem Zahlenverhältnis Ether-Brücken/Carbonyl-Brücken. Mit steigendem Anteil an Ethergruppen relativ zu den Carbonylgruppen nimmt die Reaktivität der Polyetherketon-Hauptkette für eine elektrophile Substitution (z.B. Sulfonierung) zu. Die Anzahl der einführbaren Sulfonsäuregruppen ist von der Anzahl der über Sauerstoffe verbrückten aromatischer Ringe abhängig. Nur O-Phenyl-O-Einheitenwerden unter den angegebenen Bedingungen sulfoniert, während O-Phenyl-CO-Gruppen unsulfoniert bleiben. Im allgemeinen liegt die Temperatur beim Auflösen des Polymers zwischen 10 und 60°C, insbesondere zwischen 20 und 60°C, vorzugsweise zwischen 30 und 50°C. Während dieses Lösungsprozesses ist eine Sulfonierung der Hauptkette weitgehend unterdrückt. Eigene NMR-Untersuchungen haben gezeigt, daß während der Sulfonierung kein Abbau eintritt.

Nach vollständigem Lösen der Probe wird die Konzentration der Schwefelsäure, z.B. durch Zugabe von Oleum erhöht, bis die H_2SO_4-Konzentration 98 bis 99,9, insbesondere 98 bis 99,5, vorzugsweise 98,2 bis 99,5 Gew.-% beträgt. Die Reaktionstemperatur bei der eigentlichen Sulfonierung kann höher liegen als beim

Löseprozeß. Im allgemeinen sulfoniert man bei 10 bis 100°C, insbesondere 30 bis 90°C, vorzugsweise bei 30 bis 80°C. Sowohl eine Temperaturerhöhung wie auch eine Verlängerung der Reaktionszeit bewirken eine Erhöhung des Sulfonierungsgrads des Polymers. Typische Reaktionszeiten liegen zwischen 0,5 und 10 Stunden, insbesondere zwischen 1 bis 8 Stunden, vorzugsweise zwischen 1,5 bis 3 Stunden. Reaktionszei-
5 ten über 10 Stunden erhöhen den Sulfonierungsgrad nur noch unwesentlich. Eine Erhöhung der Temperatur der Lösung auf mindestens 50°C nach Zugabe des sulfonierenden Agens beschleunigt die Sulfonierung erheblich.

Bevorzugt werden Homopolymere der allgemeinen Formeln IV oder V oder VI sulfoniert. Nach einer weiteren Ausgestaltung der Erfindung wird das beschriebene Verfahren eingesetzt zur Sulfonierung eines
10 aromatischen Polyetherketons, das ein Copolymer darstellt, und aus mindestens 2 unterschiedlichen Einheiten der allgemeinen Formel IV, V und VI

(I V)

(V)

(V I)

35 aufgebaut ist.

Eine weitere vorzugsweise Ausgestaltung des erfindungsgemäßen Verfahrens besteht darin, daß man ein Polyetherketon einsetzt, das aus Einheiten der allgemeinen Formel V oder VI und zusätzlich aus nicht sulfonierbaren Einheiten aufgebaut ist. Die Sulfonierung von Copolymeren aus Monomer-Einheiten der allgemeinen Formel IV und nichtsulfonierbaren Etherketon-Einheiten wird in EP-A-41780 und EP 08895
40 beschrieben. Bei der vollständigen Sulfonierung eines Homopolymeren der allgemeinen Formel IV würde unter den gleichen Bedingungen ein vollkommen wasserlösliches Produkt mit sehr starker Quellbarkeit in Wasser bei Raumtemperatur erhalten werden, dessen Isolierung sehr schwierig ist. Diese Eigenschaften sind z. B. für eine Anwendung der Polysulfonsäuren als hydrophile Ionenaustauschermembrane in Elektroly-sezellen unerwünscht, da eine starke Quellung zum Verlust der mechanischen Beständigkeit der Membran
45 führt. Andererseits ist aber gerade für eine hohe Ionenaustauscherkapazität ein hoher Sulfonierungsgrad erforderlich.

Auch bei diesem Verfahren wird das Polyetherketon in Schwefelsäure von 94 bis 97 Gew.-% gelöst. Die erhaltene Lösung wird mit einem sulfonierenden Agens versetzt bis die Schwefelsäurekonzentration 98 bis 99,5 Gew.-% beträgt. Der Reaktionsansatz wird aufgearbeitet, sobald der gewünschte Sulfonierungsgrad
50 erreicht ist.

Die nicht sulfonierbaren Einheiten weisen vorzugsweise die Formel VII auf

(V I I)

und leiten sich dann formal von 4-Oxy-Benzophenon ab oder besitzen die allgemeine Formel VIII
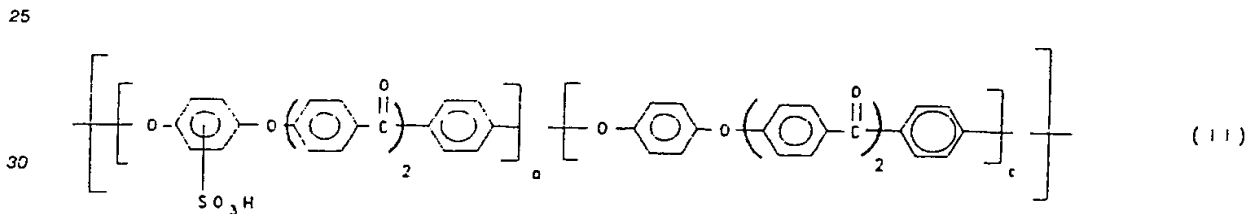
5

(V I I I)

10 und leiten sich dann von 4-Oxy-Benzosulfon ab.

Das Polymere der allgemeinen Formel IV wird in Schwefelsäure von 95 bis 96,5 Gew.-% bei maximal 25°C gelöst. Zum Lösen des Polymeren der allgemeinen Formel V in Schwefelsäure von 94 bis 96 Gew.-% arbeitet man vorzugsweise bei 30°C. Das Homopolymer der Formel VI wird vorzugsweise in Schwefelsäure von 95 bis 96,5 Gew.-% bei 25 bis 50°C gelöst und anschließend bei Temperaturen von 60 bis 15 90°C sulfoniert. Die Polymere der allgemeinen Formel I werden bei 25°C gelöst. Die eigentliche Sulfonierung findet dann bei mindestens 50°C und einer Säurekonzentration von mindestens 98,5 Gew.-% H_2SO_4 statt.

Die nach dem erfindungsgemäßen Verfahren gewonnenen aromatischen Polyaryletherketone sind teilweise neu. Sie besitzen die allgemeine Formel I, wobei jedoch mindestens 20 % der O-Phenylen-O-Einheiten (Ar) 20 mit einer SO_3H-Gruppe substituiert sind. Dabei sollen die Kombinationen p = 2, M = 0, N = 0, Y = 0, sowie p = 1, M = 1, X = 0, Y = 0, N = 0, ausgenommen sein.

Bei der Sulfonierung des Homopolymers der allgemeinen Formel VI fällt die Sulfonsäure der allgemeinen Formel II

25

30

(I I)

an, in der a eine Zahl von 0,2 bis 1, c = eine Zahl von 0 bis 0,8 bedeutet und die Summe a + c = 1 35 beträgt.

Bei der Sulfonierung des Homopolymers der allgemeinen Formel V entsteht die Sulfonsäure der allgemeinen Formel III

40

45

50

55

$$(\text{I I I})$$

in der a eine Zahl von 0 bis 1, b eine Zahl von 0 bis 1, c eine Zahl von 0 bis 0,5, bedeutet und die Summe a + b + c = 1 beträgt.

Bei der Sulfonierung werden zuerst Monosubstitutionsprodukte (b = 0) erhalten, in denen a zwischen 0,5 und 1 und c zwischen 0 und 0,5 liegt. Dann erreicht a ein Maximum (etwa 1) wobei b gering bleibt und c auf geringe Werte zurückgeht. Schließlich kommt es zur Disulfonierung und der Wert von b steigt auf Kosten von a an.

Mit steigendem Ether/Ketonverhältnis erhöht sich die Masse der Wiederholungseinheit. Dadurch wird der Anteil von SO_3H^- am Gesamtgewicht für die Polymere IV, V und VI bei gleichem Sulfonierungsgrad unterschiedlich. Beispielsweise besitzt ein sulfoniertes Polyetherketon der Formel IV mit einem Sulfonierungsgrad von 40 % ein SO_3H-Äquivalent von 1,25 mmol/g, während sulfoniertes Polyetherketon der Formel VI bei einem Sulfonierungsgrad von 40 % nur ein SO_3H-Äquivalent von 0,94 mmol/g aufweist.

Obwohl der Sulfonierungsgrad (Anteil der sulfonierten O-Phenyl-O-Einheiten) in beiden Fällen gleich ist, sind die physikalischen und mechanischen Eigenschaften unterschiedlich. Durch Variation des Ketonanteils im Polymer erreicht man neben einer geringeren Reaktivität auch eine gezieltere Einstellung eines gewünschten Eigenschaftsprofils. Das Polyetherketon der Formel VI läßt sich sehr hoch sulfonieren, ohne jedoch wasserlöslich zu werden. Bei einem Sulfonierungsgrad von 85 % wird das Polymer der Formel IV vollständig wasserlöslich, während ein sulfoniertes Polymer der Formel VI mit 85 % SO_3H-Gruppen noch handhabbar und aus Wasser isolierbar ist.

Bei gleichem Sulfonierungsgrad ist ein sulfoniertes Polymer der Formel I mit p = 2 schlechter löslich und in Wasser weniger quellbar als sulfoniertes Polymer der Formel IV

$$(\text{I V})$$

Die Sulfonsäuren der Formel II, die sich von Homopolymerisat der allgemeinen Formel VI ableiten, sind oberhalb eines Sulfonierungsgrades von 40 % löslich in DMF, N-Methylpyrrolidon, Dimethylsulfoxid und konz. Schwefelsäure. Sie sind jedoch unlöslich in 25 %iger Kalilauge, Chloroform und Tetrahydrofuran. Sowohl die eingesetzten Etherketone wie die erhaltenen Sulfonsäuren besitzen Molgewichte von mindestens 30 000.

Die Erfindung wird durch die Beispiele näher erläutert.

Beispiele:

In einer Vierhals-Rührapparatur mit Tropftrichter und Ölbad wurde 96 %ige konz. Schwefelsäure vorgelegt und unterschiedliche aromatische Polyetherketone gelöst. Danach wurde die Säurekonzentration

durch Titration mit Oleum (Gehalt 20 % SO_3) auf 98,5 bis 99,5 Gew.-% H_2SO_4 eingestellt. Die Sulfonierung wird durch eine sich anschließende Temperaturerhöhung beschleunigt. Die Endtemperatur hängt vom jeweiligen Polymer ab.

Die Versuche der Tabelle 1 wurden mit einem Homopolymer der allgemeinen Formel IV durchgeführt. Die Versuche der Tabelle 2 wurden mit einem Homopolymer der allgemeinen Formel V durchgeführt. Die Versuche der Tabelle 3 wurden mit einem Homopolymer der allgemeinen Formel VI durchgeführt.

In den Tabellen wurden folgende Abkürzungen benutzt:

Legende

LT	= Lösetemperatur
RT	= Reaktionstemperatur
RZ	= Reaktionszeit
Ausb.	= Ausbeute
inh. V.	= inhärente Viskosität in conc. H_2SO_4 bei 25°C (0,1 %) gemessen
Sulfgrad	= Sulfonierungsgrad, bestimmt durch den Schwefelgehalt aus der Elementaranalyse (Anteil der sulfonierten O-Phenylen-O-Einheiten)

Tabelle 1

	LT (°C)	Säure Endkonz (%)	RT (°C)	RZ (h)	Ausb. (%)	inh. V (dl/g)	Sulfgrad (%)
I	25	98.50	25	1.00	> 90	--	40
II	25	98.50	45-50	1.25	> 90	--	63
III	25	98.50	45-50	1.50	> 90	0.73	66
IV	40	98.50	60	3.00	> 90	0.64	82
V	25	98.50	50	1.50	> 90	0.71	77
VI	25	98.50	50	1.50	> 90	0.71	76

Tabelle 2

	LT (°C)	Säure Endkonz (%)	RT (°C)	RZ (h)	Ausb. (%)	inh. V (dl/g)	Sulfgrad (%)
I	30	98.50	30-35	1.25	> 90	0.77	50
II	30	98.50	25-30	6.00	> 90	0.74	60
III	30	98.50	50	1.00	> 90	0.76	46
IV	30	98.20	50	4.00	> 90	0.67	69

Tabelle 3

	LT (°C)	Säure Endkonz (%)	RT (°C)	RZ (h)	Ausb. (%)	inh. V (dl/g)	Sulfgrad (%)
I	45	98.30	60	1.00	> 90	0.80	21
II	45	98.30	70	0.50	> 90	0.80	31
III	45	98.30	80	0.50	> 90	0.71	52
IV	45	98.30	80	1.50	> 90	0.67	72
V	45	98.50	60	4.00	> 90	0.80	28
VI	45	99.10	80	4.00	> 90	0.60	81
VII	45	99.95	60	4.00	> 90	0.69	82
VIII	45	99.95	80	6.00	> 90	0.57	75
IX	45	98.40	80	3.00	> 90	0.70	91
X	45	99.10	60	1.00	> 90	0.62	76
XI	45	99.95	60	0.83	> 90	0.70	57

Patentansprüche

1. Polymerelektrolyt bestehend aus einem sulfonierten aromatischen Polyetherketon der allgemeinen Formel I

bei denen mindestens 20 % der O-Phenylen-O-Einheiten mit einer SO_3H-Gruppe substituiert sind, wobei

Ar   einen Phenylenring mit p- und/oder m-Bindungen,
Ar'   eine Phenylen-, Naphthylen-, Biphenylylen, Anthrylen- oder eine andere zweiwertige aromatische Einheit,
X, N und M unabhängig voneinander 0 oder 1,
Y   0, 1, 2 oder 3,
P   1, 2, 3 oder 4

bedeutet, wobei die Kombinationen P = 2, M = 0, N = 0, Y = 0 und P = 1, M = 1, X = 0, Y = 0, N = 0 ausgenommen sein sollen.

2. Polymerelektrolyt gemäß Anspruch 1, dadurch gekennzeichnet, daß er die allgemeine Formel II

(II)

besitzt, wobei
a = 0.2 - 1,
c = 0 - 0.8 bedeutet und
a + c = 1 ist.

3. Polymerelektrolyt gemäß Anspruch 1, dadurch gekennzeichnet, daß er die allgemeine Formel III
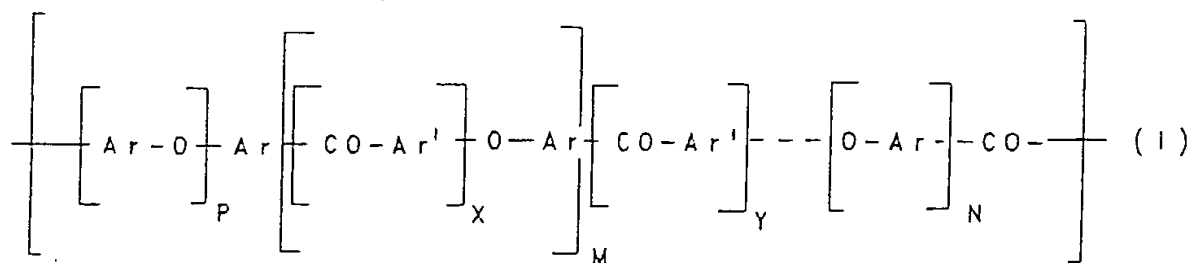

(III)
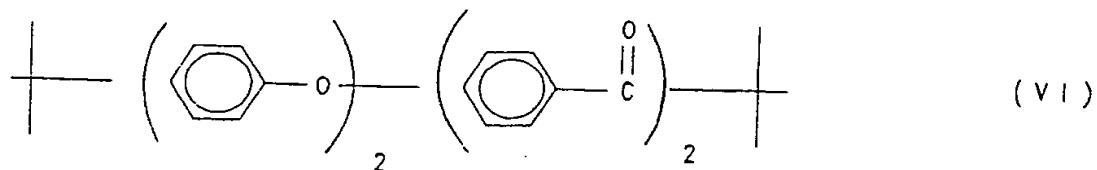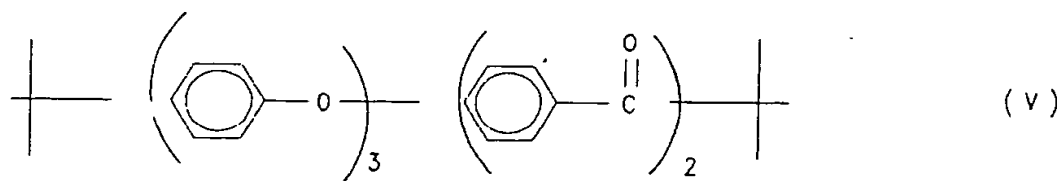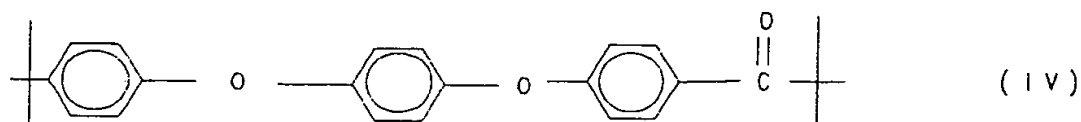

besitzt, wobei
a = 0 - 1,
b = 0 - 1,
c = 0 - 0.5 und
a + b + c = 1 beträgt.

4. Verfahren zur Herstellung eines Polymerelektrolyten durch Sulfonierung eines aromatischen Polyether-ketons der allgemeinen Formel I
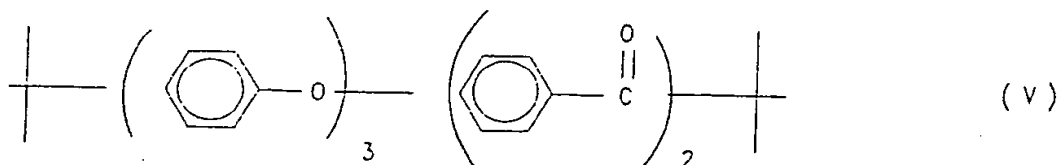
$$\left[\begin{array}{c}\left[Ar-O\right]_P Ar\left[\begin{array}{c}\left[CO-Ar'\right]_X O-Ar'\end{array}\right]_M\left[CO-Ar'\right]_Y - - \left[O-Ar\right]_N-CO-\end{array}\right] \quad (\,I\,)$$

wobei P, X, M, Y, N, Ar und Ar' die in Anspruch 1 angegebene Bedeutung besitzen, dadurch gekennzeichnet, daß man das Polyetherketon in Schwefelsäure von 94 bis 97 Gew.-% löst und man die erhaltene Lösung mit einem sulfonierenden Agens versetzt, bis die Schwefelsäure-Konzentration 98 bis 99,9 Gew.-% beträgt und man den Reaktionsansatz aufarbeitet, sobald der gewünschte Sulfonierungsgrad erreicht ist.

5. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, daß in Formel I der Rest Ar' ausschließlich für Phenylen steht.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß man ein aromatisches Polyetherketon einsetzt, das ein Copolymer darstellt, das aus mindestens zwei unterschiedlichen Einheiten der Formeln IV, V und VI

$$(\,IV\,)$$

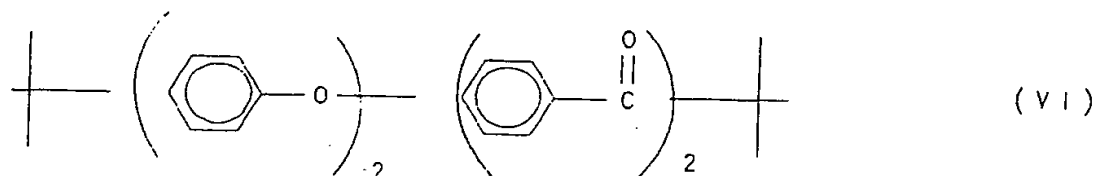

$$(\,V\,)$$

$$(\,VI\,)$$

aufgebaut ist.

7. Verfahren zur Herstellung eines Polymerelektrolyten durch Sulfonierung eines aromatischen Polyetherketons in Schwefelsäure, dadurch gekennzeichnet, daß man ein Polyetherketon einsetzt, das aus Einheiten der Formel
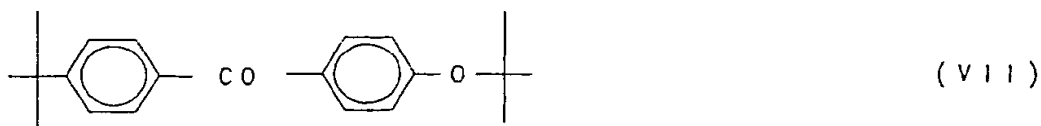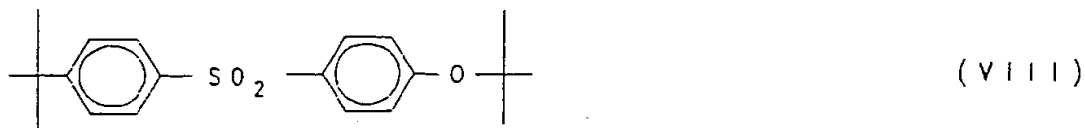
$$\left. \underset{}{\text{—}} \left(\underset{3}{\bigcirc - O} \right) \text{—} \left(\underset{2}{\bigcirc - \overset{\overset{O}{\|}}{C}} \right) \right. \qquad (V)$$

o d e r

$$\left. \underset{}{\text{—}} \left(\underset{2}{\bigcirc - O} \right) \left(\underset{2}{\bigcirc - \overset{\overset{O}{\|}}{C}} \right) \right. \qquad (V\,I)$$

sowie aus nicht sulfonierbaren Einheiten aufgebaut ist, man das Polyetherketon in Schwefelsäure von 94 bis 97 Gew.-% löst und man die erhaltene Lösung mit einem sulfonierenden Agens versetzt, bis die Schwefelsäure-Konzentration 98 bis 99,5 Gew.-% beträgt und man den Reaktionsansatz aufarbeitet, sobald der gewünschte Sulfonierungsgrad erreicht ist.

8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß man ein aromatisches Polyetherketon einsetzt, dessen nicht sulfonierbare Einheiten die Formel VII
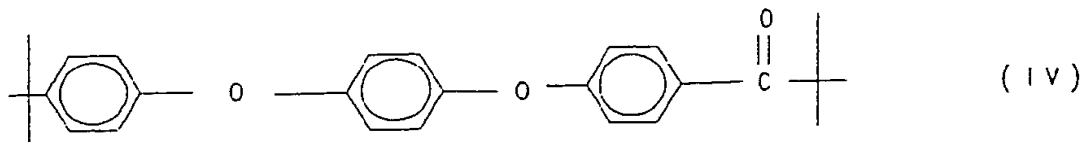
$$\left. \underset{}{\text{—}} \bigcirc \text{— C O —} \bigcirc \text{— O} \right. \qquad (V\,I\,I)$$

aufweisen.

9. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß man ein aromatisches Polyetherketon einsetzt, dessen nicht sulfonierbare Einheiten die Formel VIII

$$\left. \underset{}{\text{—}} \bigcirc \text{— S O}_2 \text{—} \bigcirc \text{— O} \right. \qquad (V\,I\,I\,I)$$

aufweisen.

10. Verfahren nach Anspruch 4 oder 7, dadurch gekennzeichnet daß das sulfonierende Agens ausgewählt ist aus rauchender Schwefelsäure, Chlorsulfonsäure und Schwefeltrioxid.
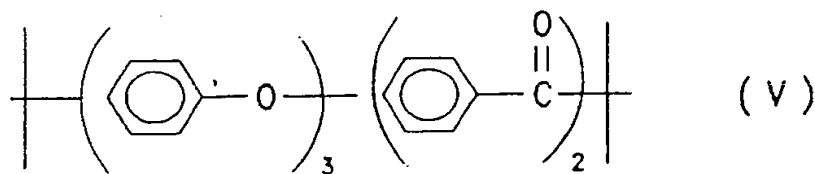
11. Verfahren nach Anspruch 4 oder 7, dadurch gekennzeichnet, daß man nach Zugabe des sulfonierenden Agens die Temperatur der Lösung auf mindestens 50° C erhöht, um die Sulfonierung zu beschleunigen.

12. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, daß man ein Polymeres der allgemeinen Formel IV
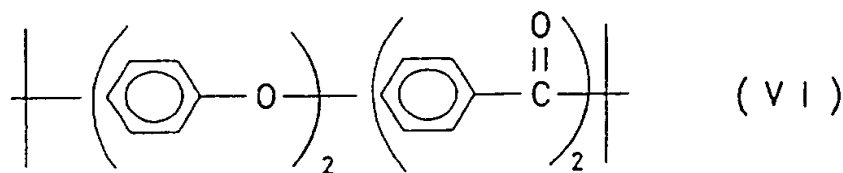
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$$+\left[\bigcirc\!\!\!\!\bigcirc - O - \bigcirc\!\!\!\!\bigcirc - O - \bigcirc\!\!\!\!\bigcirc - \overset{\overset{\textstyle O}{\|}}{C}\right]+ \qquad (\,I\,V\,)$$

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in Schwefelsäure von 95 bis 96,5 Gew.-% bei maximal 25 ˙ C löst.

13. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, daß man ein Polymeres der allgemeinen Formel V,

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$$+\left(\bigcirc\!\!\!\!\bigcirc - O\right)_3\!\!\left(\bigcirc\!\!\!\!\bigcirc - \overset{\overset{\textstyle O}{\|}}{C}\right)_2\!\!+ \qquad (\,V\,)$$

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in Schwefelsäure von 94 bis 96 Gew.-% bei 25 ˙ C löst.

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14. Verfahren gemäß Anspruch 4, dadurch gekennzeichnet, daß man ein Polymeres der allgemeinen Formel VI

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$$+\left(\bigcirc\!\!\!\!\bigcirc - O\right)_2\!\!\left(\bigcirc\!\!\!\!\bigcirc - \overset{\overset{\textstyle O}{\|}}{C}\right)_2\!\!+ \qquad (\,V\,I\,)$$

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in Schwefelsäure von 95 bis 96,5 Gew.-% bei Temperaturen von 25 bis 50 ˙ C löst und bei Temperaturen von 60 bis 90 ˙ C sulfoniert.

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EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int. Cl.5)
A,D	MACROMOLECULES Bd. 18, 1985, Seiten 86 - 93 BISHOP M.T. ET AL 'Solubility and properties of a poly(aryl ether ketone) in strong acids' * Seite 86, Spalte 2, Zeile 10 - Zeile 16 *	1-14	C08G65/48 H01M6/18 H01M10/40
A	EP-A-0 382 440 (ICI) * Anspruch 1 *	1-14	
A	US-A-2 861 116 (GRUBB W.T.) * Anspruch 1 * * Spalte 3, Zeile 63 - Zeile 67 * * Spalte 3, Zeile 74 *	1-14	
A	PATENT ABSTRACTS OF JAPAN vol. 14, no. 288 (E-943)(4231) 21. Juni 1990 & JP-A-29 4 261 (SAKOTA KAGAKU KAIHATSU KENKYUSHO K.K.) 5. April 1990 * Zusammenfassung *	1-14	
			RECHERCHIERTE SACHGEBIETE (Int. Cl.5)
A	EP-A-0 047 903 (BASF) * Seite 3, Zeile 1 - Zeile 5 *	9	C08G H01M

Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt

Recherchenort	Abschlußdatum der Recherche	Prüfer
DEN HAAG	21 SEPTEMBER 1993	O'SULLIVAN T.P.

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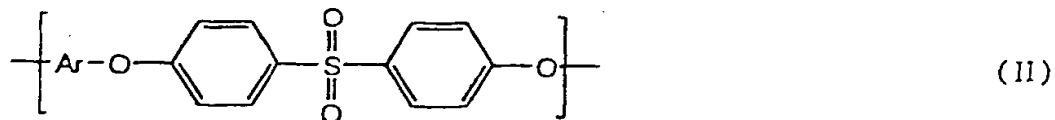• Iwasaki, Katsuhiko
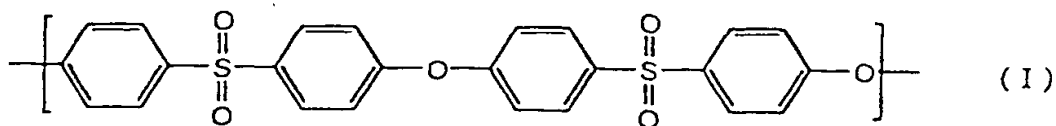Niihama-shi, Ehime (JP)
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(54)   Polymer electrolyte for fuel cell

(57)   Provided is a polymer electrolyte which is cheap and easily synthesized, and has a high water resistance and high output performance.

The polymer electrolyte comprising a sulfonated polymer having an ion-exchange group equivalent weight of 500 to 2500 g/mol, which is obtainable by sulfonating a structural unit represented by the structural formula (II) of a copolymer having 95 to 40 mol% of a structural unit represented by the following structural formula (I) and 5 to 60 mol% of a structural unit represented by the following structural formula (II),

EP 0 932 213 A1

Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001]   The present invention relates to a polymer electrolyte for a fuel cell, a method for producing them, and a fuel cell.

Description of the Related Art

[0002]   Due to the recent attention to various environmental problems, a new energy technique has thus attracted special interests. It is such a fuel cell technique which is considered a promising new energy technique and it is anticipated that it will become one of the most important technology in the future. A polymer type fuel cell using a proton-conductive polymer as an electrolyte has attracted such special interest because of features such as good operation property at low temperatures, possibility of miniaturization and creating light, etc.

[0003]   As a polymer electrolyte for a polymer type fuel cell, for example, Nafion (trademark of Du Pont Co.) having ultrastrong acid group containing fluorinated polymer is known. However, Nafion is very expensive because it is a fluorinated polymer, and control of water must be strictly followed because of its low water retention in the case of using it as a fuel cell. Furthermore, it is necessary when using a fluorine containing compound to take the environment into consideration in respect to synthesis and disposal. Therefore, a polymer electrolyte of a non-fluorinated proton-conductive material is desirable by today's market standard.
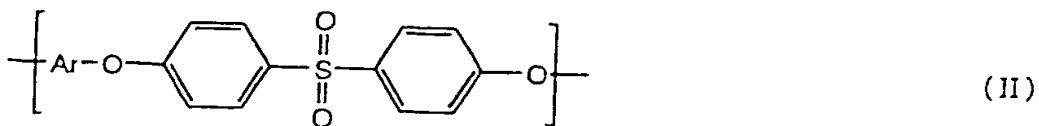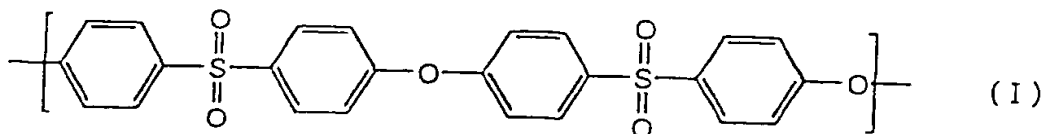
[0004]   Some studies have already been made with respect to the non-fluorinated polymer-based proton-conductive polymer,. For example, a fuel cell using a sulfonated aromatic polyether ether ketone as the electrolyte has been researched. A detailed report on the synthesis of the sulfonated aromatic polyether ether ketone and its characteristics are disclosed in Polymer, 1987, Vol. 28, 1009. This report discloses that an aromatic polyether ether ketone, which is insoluble in organic solvent, becomes soluble in an organic solvent by highly sulfonating it, thereby facilitating film formation. The hydrophilic nature of these sulfonated aromatic polyether ketone has increased thus the water-solubility or a reduction in strength on water absorption occurred. When the water-solubility occurs, a fuel cell normally forms water as a by-product as a result of a reaction between fuel and oxygen, the sulfonated aromatic polyether ketone is therefore not suitable to use as an electrolyte for a fuel cell. The Japanese Patent Kokai Publication No. 6-93114 with respect to an electrolyte of a sulfonated aromatic polyether ether ketone shows that the inventors succeeded in the production of an electrolyte having excellent strength through a process of introducing a crooslinkable functional group at the time of polymer synthesis and crosslinking this functional group after film formation.

[0005]   Polymeric Material Science and Engineering, 68, 122-123 (1993) and U.S. Patent No. 5,271,813 disclose that sulfonated compounds of polymers (e.g. sulfonated aromatic polyether ether ketone, sulfonated aromatic polyether sulfone, etc.) can be utilized as an electrolyte of a device for electrolysis of water (UDEL P-1700 used as polyether sulfone is a polymer classified as polysulfone (PSF)). However, there is no description about various physical properties such as primary structure or ion-exchange group equivalent weight of these sulfonated compounds of polymers, and it is difficult for the resulting sulfonated polysulfone not to dissolve in water due to its high water absorption.
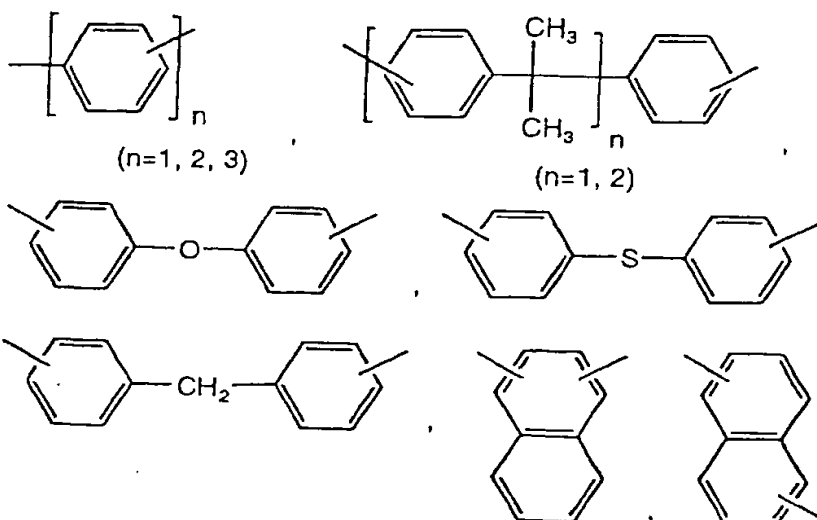
[0006]   These conventional techniques have problems such as expensive electrolyte, insufficient strength, difficult synthesis of a polymer material, etc.

SUMMARY OF THE INVENTION

[0007]   An object of the present invention is to provide a polymer electrolyte for fuel cell, which is cheap and is easily synthesized with a high water resistance and a high performance. That is, the present invention provides a polymer electrolyte for a fuel cell, comprising a sulfonated polymer having an ion-exchange group equivalent weight of 500 to 2500 g/mol, which is obtainable by sulfonating a structural unit represented by the structural formula (II) of a copolymer having 95 to 40 mol% of a structural unit represented by the following structural formula (I) and 5 to 60 mol% of a structural unit represented by the following structural formula (II); a polymer electrolyte membrane for a fuel cell, comprising the polymer electrolyte for a fuel cell; and a fuel cell using the polymer electrolyte membrane for fuel cell,

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(I)

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(II)

wherein Ar represents at least one of the following structures,

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(n=1, 2, 3) ,

(n=1, 2) ,

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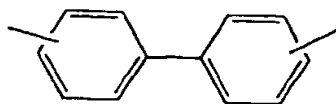## BRIEF DESCRIPTION OF THE DRAWING

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[0008]

Fig. 1 is a plot of current density versus voltage illustrating a fuel cell output performance in Examples and Comparative Example.

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DETAILED DESCRIPTION OF THE INVENTION

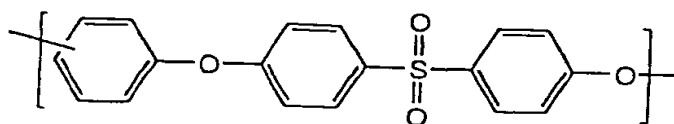[0009] The present invention will be described in detail hereinafter.

[0010] The polymer electrolyte for a fuel cell of the present invention comprises a sulfonated polymer having an ion-exchange group equivalent weight of 500 to 2500 g/mol, which is obtainable by sulfonating a structural unit represented only by the structural formula (II) of a copolymer having 95 to 40 mol% of a structural unit represented by the above structural formula (I) and 5 to 60 mol% of a structural unit represented by the above structural formula (II).

[0011] In the structural unit represented by the structural formula (II) in the polyether sulfone copolymer, Ar is a divalent aromatic group, and preferably has the following structure.

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[structural formula - biphenyl structure]

[0012] As a method of synthesizing the polyether sulfone copolymer, for example, a method described in Japanese Patent Kokoku Publication No. 62-28169 is known. A molecular weight of the polymer is not specifically limited, but a weight-average molecular weight is preferably from 5,000 to 200,000, more preferably from 10,000 to 100,000. When the molecular weight is smaller than 5,000, the strength of the film obtained after film formation may be decreased. On the other hand, when the molecular weight is larger than 200,000, it sometimes becomes difficult to perform molding processing.

[0013] As a method of sulfonating the polyether sulfone copolymer, i.e. method of introducing a sulfonic acid group into a polymer, for example, methods described in Japanese Patent Kokoku Publication Nos. 61-36781, 2-17571 and 1-54323 are known. In Japanese Patent Kokoku Publication No. 61-36781, there is described a method of sulfonating a copolymer having a structural unit represented by the above structural formula (I) and a structural unit represented by the following structural formula (III) with concentrated sulfuric acid. Specifically, it is described that the structural unit represented only by the following structural formula (III) can be selectively sulfonated by dissolving the copolymer in concentrated sulfuric acid and stirring at room temperature for several hours.

[structural formula (III)] (III)

[0014] A sulfonating agent used for sulfonating the polyether sulfone copolymer of the present invention is not specifically limited, but concentrated sulfuric acid capable of sulfonating the structural unit represented only by the above structural unit (II) selectively and quantitatively, is preferable.

[0015] The polymer electrolyte for a fuel cell of the present invention comprises a sulfonated polymer having an ion-exchange group equivalent weight of 500 to 2500 g/mol, which is obtainable by sulfonating the structural unit represented only by the above structural formula (II) of the polyether sulfone copolymer. The ion-exchange group equivalent weight is preferably from 550 to 1500 g/mol, more preferably from 600 to 1000 g/mol. When the ion-exchange group equivalent weight exceeds 2500 g/mol, the output performance is decreased. On the other hand, when the ion-exchange group equivalent weight is lower than 500 g/mol, the water resistance of the copolymer is decreased.

[0016] The term "ion-exchange group equivalent weight" used herein means a molecular weight of the sulfonated polymer per mol of sulfonic acid groups introduced, i.e. amount of sulfonic acid groups introduced. The ion-exchange group equivalent weight can be measured, for example, by an acid base titration method described in Japanese Patent Kokoku Publication No. 1-52866.

[0017] As a method of controlling the ion-exchange group equivalent weight of the sulfonated polyether sulfone copolymer in the range from 500 to 2500 g/mol, a method of controlling a copolymerization ratio of the structural unit represented by the structural formula (I) to the structural unit represented by the structural formula (II) of the polyether sulfone copolymer can be used.

[0018] In case of sulfonating the polyether sulfone copolymer, a sulfonic acid group ($-SO_3H$) is substantially introduced only into an aromatic ring which is not adjacent to a sulfone group ($-SO_2-$) in the structural unit represented by the above structural formula (II), i.e. the unit represented by Ar. The number of sulfonic acid groups to be introduced is at most one per one aromatic ring when the bond position in the polymer backbone chain of the aromatic ring is ortho- or para-position. When the aromatic ring is bonded in the polymer backbone chain at the meta-position, the number of sulfonic acid groups is at most two per one aromatic ring. Therefore, sulfonated polymer having different sulfonation degree (ion-exchange group equivalent weight) can be obtained from polymers having the same molecular weight according to the bond position of the aromatic ring in the polymer backbone chain.

[0019] That is, in the present invention, when the ion-exchange group equivalent weight of the desired sulfonated polymer is decided, the desired sulfonated polymer can be obtained by selecting or synthesizing the polyether sulfone copolymer having the specific bond position of the Ar in the polymer backbone chain unit and quantitatively sulfonating

the copolymer.

[0020]   When a polymer electrolyte is used for a fuel cell, it is normally used in the form of a film. A method of converting the sulfonated polymer into a film is not specifically limited, but a method of forming a film from a solution state (solution casting method) or a method of forming a film from a molten state (melt pressing method or melt extrusion method) can be used. In case of the former, for example, a film is formed by casting and applying a N,N-dimethylformamide solution of a polymer on a glass plate, and removing the solvent. The solvent used for forming a film may be any one which can dissolves the polymer and is removed after coating. For example, there can be suitably used aprotic polar solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, dimethylsulfoxide, etc.; or alkylene glycol monoalkyl ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, etc.

[0021]   A thickness of the film is not specifically limited, but is preferably from 10 to 200 μm. In order to obtain the film strength enough for practical use, the thickness is preferably thicker than 10 μm. In order to reduce the film resistance, i.e. improvement in output performance, the thickness is preferably thiner than 200 μm. The film thickness can be controlled by the solution concentration or thickness of coating onto the substrate. In case of forming a film from a molten state, a melt pressing method or a melt extrusion method can be used.

[0022]   In case of producing the electrolyte of the present invention, there can be used additives such as plasticizers, stabilisers, releasants, etc., as far as the object of the present invention is not adversely affected.

[0023]   A method of bonding the electrolyte to an electrode in case of using for a fuel cell is not specifically limited, and a known method (e.g. chemical plating method described in Denki Kagaku, 1985, 53, 269, thermal press method of a gas diffusion electrode described in Electrochemical Science and Technology, 1988, 135 (9), 2209, etc.) can be applied.

EXAMPLES

[0024]   The following Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof. The measuring conditions of the respective physical properties are as follows.

(1) Ion-exchange group equivalent weight

[0025]   After precisely weighing (a (g)) a sulfonated polymer to be measured in a closable glass container, an excess amount of an aqueous calcium chloride solution is added therein, followed by stirring overnight. Hydrogen chloride generated in the system is titrated (b (ml)) with an aqueous 0.1 N standard sodium hydroxide solution (potency: f) using phenolphthalein as an indicator. An ion-exchange group equivalent weight (g/mol) is determined from the above measured value according to the following equation.

$$\text{Ion-exchange group equivalent weight} = (1000 \times a)/(0.1 \times b \times f)$$

(2) Output performance of a fuel cell

[0026]   An electrolyte bonded with an electrode was incorporated into a cell to be evaluated, and the output performance of a fuel cell was evaluated. As a reaction gas, hydrogen/oxygen was used. After moistening by passing through a water bubbler at 23°C under a pressure of 1 atm, the reaction gas was fed to the cell to he evaluated. A flow rate of hydrogen and that of oxygen were adjusted to 60 ml/min. and 40 ml/min., respectively. A cell temperature was adjusted to 23°C. The output performance of the cell was evaluated by using a charge/discharge test unit (H201B, manufactured by Hokuto Denko Co., Ltd.).

Example 1

(1) Production of a polyether sulfone copolymer

[0027]   A polyether sulfone copolymer using 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxybiphenyl and 4,4'-dichlorodiphenyl sulfone as a monomer was prepared by reacting 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxybiphenyl and 4,4'-dichlorodiphenyl sulfone in a ratio of 6:4:10 in the presence of potassium carbonate, using diphenyl sulfone as a polymerization solvent. The polymerization temperature was in the range from 200 to 290°C. The whole diol and dihalide as a substantially equimolar component were used, together with a two-fold excess molar equivalent of potassium carbonate to the molar equivalent of dihalide. It was confirmed by ^{1}H-NMR that a copolymer having a composition ratio corresponding to the charged raw materials, wherein the ratio of the structural unit represented by the above structural formula (I) to that represented by the above structural formula (II) is 6:4, is obtained. A reduced viscosity of the resulting

polymer in 1% N,N-dimethylformamide solution at 25°C was 0.38, and weight-average molecular weight (in terms of polystyrene) of the resulting polymer determined by gel permeation chromatography (GPC) was 55,000.

(2) Sulfonation of polyether sulfone copolymer

[0028] The polyether sulfone copolymer (25 g) obtained in the above item (1) and concentrated sulfuric acid (125 ml) were charged in a 500 ml round bottom flask equipped with a thermometer, a nitrogen introducing tube, a dropping funnel and a stirrer, and then the polymer was sulfonated by stirring at room temperature under a nitrogen flow overnight. The sulfonated polyether sulfone was precipitated by slowly adding the reaction solution to 3 liter of deionized water, filtered and then recovered. A deionized water-washing operation using a mixer and a recovering operation using a suction filter were repeated until the wash becomes neutral, and then the polymer was dried under reduced pressure at 80°C overnight.
[0029] The ion-exchange group equivalent weight of the resulting sulfonated polyether sulfone was 660 g/mol. It was confirmed by the results of the titration of the polymer after sulfonation and measurement of ^{1}H-NMR that the sulfonic acid group is introduced into only a 4,4'-dihydroxybiphenyl unit in the polymer backbone chain, selectively and quantitatively.

(3) Evaluation of a fuel cell

[0030] The sulfonated polyether sulfone copolymer obtained in the above item (2) dissolved in N-methyl-2-pyrrolidone was casted and applied on a glass substrate, dried under reduced pressure while slowly decreasing pressure at 80°C, followed by heating to 150°C and further drying under reduced pressure for 3 hours to completely remove the solvent. The resulting film was a pale brown transparent flexible film and had a thickness of 140 μm. The film was punched out to form a circle having a diameter of 30 mm Ø and a gas diffusion electrode was thermally press-bonded, and the resultant was used for evaluation of a fuel cell. As the gas diffusion electrode, a Pt-supporting (0.35 mg/cm^2) electrode manufactured by E-TEK U.S.A. Inc. was used. The punched gas diffusion electrode having a diameter of 20 mm Ø was uniformly impregnated with 0.1 ml of a 5 wt% Nafion solution (lower alcohol/water mixed solvent, manufactured by Aldrich U.S.A. Inc.) as a binder and then dried under reduced pressure at 80°C for 2 hours to remove the solvent. The electrode was immersed in boiling deionized water for 2 hours, together with the electrolyte film, thereby to let the binder portion absorb water. They were taken out from water and, after removing water adsorbed on the surface, the electrolyte film was interposed between two electrodes so that the catalyst surface of the electrode faces the electrolyte side, followed by pressing at 80°C under 80 kgf/cm^2 for 90 seconds to obtain an electrode-bonded membrane. The resulting electrode-bonded membrane was incorporated into the cell to be evaluated and the output performance of the fuel cell was evaluated. The resulting plot of current density versus voltage is shown in Fig. 1.

Example 2

(1) Evaluation of fuel cell

[0031] A film of the sulfonated polyether sulfone copolymer obtained in Example 1(2) was formed by using a thermal press molding device. The polymer powder (0.5 g) and an aluminum spacer having a width of 0.2 mm and an inner diameter of 30 mm Ø were interposed between two Teflon sheets having a thickness of 0.2 mm and, furthermore, the resultant laminate was interposed between two steel plates having a thickness of 3 mm. After heating at 280°C under 5 kgf/cm^2 for 3 minutes and thermal press molding at 280°C under 200 kgf/cm^2 for 2 minutes, a film having a thickness of 200 μm was obtained. According to the same manner as that described in Example 1(3), an electrode was bonded and the output performance of the cell was evaluated. As a result, the cell showed the same output performance as that of Example 1.

Example 3

(1) Production of polyether sulfone copolymer

[0032] According to the same manner as that described in Example 1 except for changing the ratio of 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxybiphenyl and 4,4'-dichlorodiphenyl sulfone to 7:3:10, a polyether sulfone copolymer was prepared. It was confirmed by ^{1}H-NMR that a copolymer having a composition ratio corresponding to the charged raw material, wherein the ratio of the structural unit represented by the above structural formula (I) to that represented by the above structural formula (II) is 7:3, is obtained. A reduced viscosity of the resulting polymer in a 1% N,N-dimethylformamide solution at 25°C was 0.39, and a weight-average molecular weight (in terms of polystyrene) of the resulting

polymer determined by GPC was 57,000.

(2) Sulfonation of polyether sulfone copolymer

[0033] According to the same manner as that described in Example 1(2), the polyether sulfone copolymer obtained in the above item (1) was sulfonated to obtain a sulfonated polyether sulfone having an ion-exchange group equivalent weight of 860 g/mol. It was confirmed by the results of the titration of the polymer after sulfonation and measurement of ^{1}H-NMR that the sulfonic acid group is introduced into only a 4,4'-dihydroxybiphenyl unit in the polymer backbone chain, selectively and quantitatively.

(3) Evaluation of fuel cell

[0034] According to the same manner as that described in Example 1 (3), a film of the polymer was formed (pale brown transparent, 120 μm in thickness) and, after bonding a gas diffusion electrode, the output performance of fuel cell was evaluated. As a result, the cell was operated as the fuel cell in the same manner as in Examples 1 and 2. A potential of the cell was 0.7 V at a current density of 10 mA/cm^2.

Example 4

(1) Production of polyether sulfone copolymer

[0035] According to the same manner as that described in Example 1 except for changing the ratio of 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxybiphenyl and 4,4'-dichlorodiphenyl sulfone to 9:1:10, a polyether sulfone copolymer was prepared. It was confirmed by ^{1}H-NMR that a copolymer having a composition ratio corresponding to the charged raw material, wherein the ratio of the structural unit represented by the above structural formula (I) to that represented by the above structural formula (II) is 9:1, is obtained. A reduced viscosity of the resulting polymer in 1% N,N-dimethylformamide solution at 25°C was 0.38, and weight-average molecular weight (in terms of polystyrene) of the resulting polymer determined by GPC was 54,000.

(2) Sulfonation of polyether sulfone copolymer

[0036] According to the same manner as that described in Example 1(2), the polyether sulfone copolymer obtained in the above item (1) was sulfonated to obtain a sulfonated polyether sulfone having an ion-exchange group equivalent weight of 2500 g/mol.

(3) Evaluation of fuel cell

[0037] According to the same manner as that described in Example 1 (3), a film of the polymer was formed (pale brown transparent, 100 μm in thickness) and, after bonding a gas diffusion electrode, the output performance of fuel cell was evaluated. The resulting plot of current density versus voltage is shown in Fig. 1. As a result, the cell was operated as the fuel cell.

Comparative Example 1

(1) Production of polyether sulfone copolymer

[0038] According to the same manner as that described in Example 1 except for changing the ratio of 4,4'-dihydroxydiphenyl sulfone, 4,4'-dihydroxybiphenyl and 4,4'-dichlorodiphenyl sulfone to 3:7:10, a polyether sulfone copolymer was prepared. It was confirmed by ^{1}H-NMR that a copolymer having a composition ratio corresponding to the charged raw material, wherein the ratio of the structural unit represented by the above structural formula (I) to that represented by the above structural formula (II) is 3:7, is obtained. A reduced viscosity of the resulting polymer in 1% N,N-dimethylformamide solution at 25°C was 0.37, and weight-average molecular weight (in terms of polystyrene) of the resulting polymer determined by GPC was 52,000.

(2) Sulfonation of polyether sulfone copolymer

[0039] According to the same manner as that described in Example 1(2), the polyether sulfone copolymer obtained in the above item (1) was sulfonated. As a result, a polymer which is insoluble in water could not be obtained. An ion-

exchange group equivalent weight calculated on the assumption that only the structural unit represented by the above structural formula (I) is sulfonated was 400 g/mol.

Comparative Example 2

[0040]   Using a Nafion 117 film (film thickness: 180 μm) as the electrolyte film, the output performance of the fuel cell was evaluated. The Nafion film was punched out to form a cycle having a diameter of 30 mm Ø, immersed in aqueous 5% hydrogen peroxide at 100°C for 30 minutes and 5% dilute sulfuric acid at 100°C for 30 minutes, and then sufficiently washed with deionized water at 100°C. According to the same manner as that described in Example 1(3), a gas diffusion electrode was bonded to the film after washing and the output performance of the cell was evaluated. The resulting plot of current density versus voltage is shown in Fig. 1.

Comparative Example 3

(1) Sulfonation of polyether sulfone homopolymer

[0041]   A sulfonated compound of the polyether sulfone composed only of the structural unit represented by the above structural formula (I) was synthesized and the evaluation as the polymer electrolyte for fuel cell was performed as follows. Polyether sulfone Sumika Excel PES5200P (reduced viscosity of 1% N,N-dimethylformamide solution at 25°C = 0.52) was dried under reduced pressure overnight. Dried polyester sulfone (25 g) and 125 ml of concentrated sulfuric acid were charged in a 500 ml round bottom flask equipped with a thermometer, a nitrogen introducing tube, a dropping funnel and a stirrer, and then stirred at room temperature under a nitrogen flow overnight to form an uniform solution (apart from the polyether sulfone copolymer, a polyether sulfone homopolymer is not sulfonated by concentrated sulfuric acid). To this solution, 48 ml of chlorosulfuric acid was added from the dropping funnel while stirring under a nitrogen flow. Since chlorosulfuric acid reacts vigorously with water in concentrated sulfuric acid to gas evolution for a while after the initiation of the dropwise addition, chlorosulfuric acid was slowly added dropwise. After the gas evolution becomes mild, the dropwise addition was terminated within 5 minutes. The reaction solution obtained after the completion of the dropwise addition was stirred at 35°C for 5 hours to sulfonate the polyether sulfone. The sulfonated polyether sulfone was precipitated by slowly adding the reaction solution to 3 liter of deionized water, filtered and then recovered. A deionized water-washing operation using a mixer and a recovering operation using a suction filter were repeated until the wash becomes neutral, and then the polymer was dried under reduced pressure at 80°C overnight. The ion-exchange group equivalent weight of the resulting sulfonated polyether sulfone was 720 g/mol.
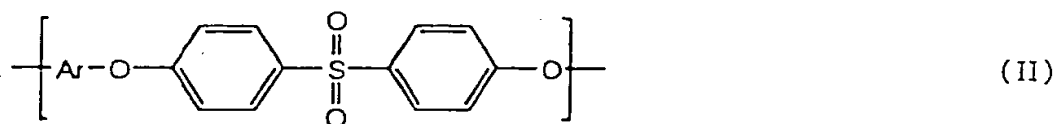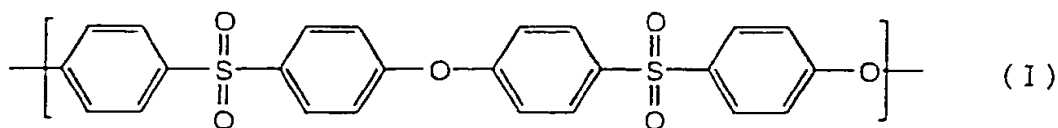
(2) Evaluation of fuel cell

[0042]   According to the method described in Example 1 (3), a film of the sulfonated polyether sulfone obtained in the above item (1) was formed. According to the same manner as that described in Example 1 (3), a trial of bonding an electrode was made, but the resulting film was completely dissolved in boiling water during a boiling water treatment. As seen from these results, the film of Example 1 has higher water resistance than that of Comparative Example 3 regardless of the introduction amount of sulfonic acid groups of Example 1 is larger than that of the Comparative Example 3. The film of Example 1 is more preferable as the polymer electrolyte for fuel cell.
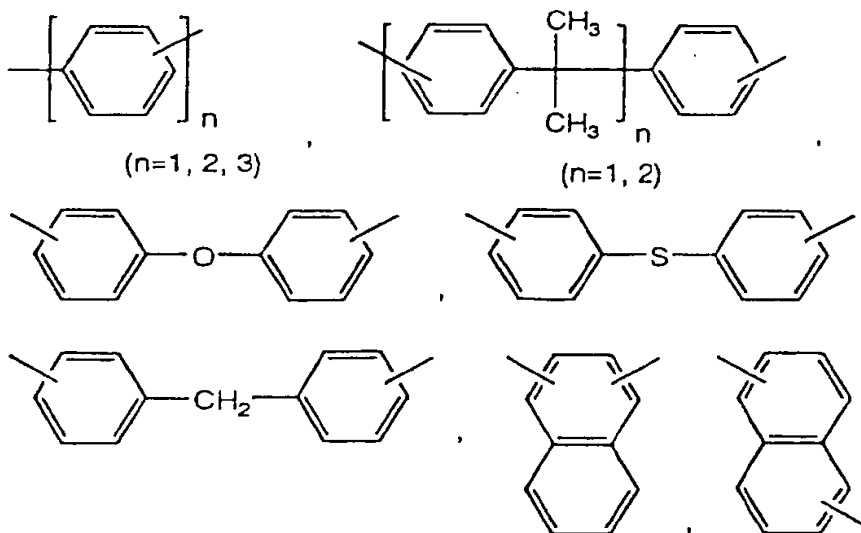
[0043]   As described above, according to the present invention, there can be provided a polymer electrolyte for fuel cell, which is cheap and easily synthesized and which has high water resistance and high output performance, a method for producing the same, and a fuel cell using the polymer electrolyte.

Claims

1.   A polymer electrolyte for a fuel cell, comprising a sulfonated polymer having an ion-exchange group equivalent weight of 500 to 2500 g/mol, which is obtainable by sulfonating a structural unit represented by the structural formula (II) of a copolymer having 95 to 40 mol% of a structural unit represented by the following structural formula (I) and 5 to 60 mol% of a structural unit represented by the following structural formula (II).
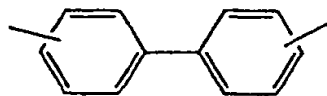
(I)

(II)

wherein Ar represents at least one of the following structures,

(n=1, 2, 3)

(n=1, 2)

2. The polymer electrolyte for a fuel cell according to claim 1, wherein the polyelrctrolyte comprises a sulfonated polymer having an ion-exchange group equivalent weight of 500 to 1500 g/mol.

3. The polymer electrolyte for a fuel cell according to claim 1 or 2, wherein Ar represents the following structure,

4. The polymer electrolyte for a fuel cell according to any one of claims 1 to 3, wherein the polymer electrolyte is obtained by controlling a copolymerization ratio of the structural formula (II) to the structural formula (I).

5. A polymer electrolyte membrane for a fuel cell, wherein the membrane comprises the polymer electrolyte for fuel cell of any one of claims 1 to 3.
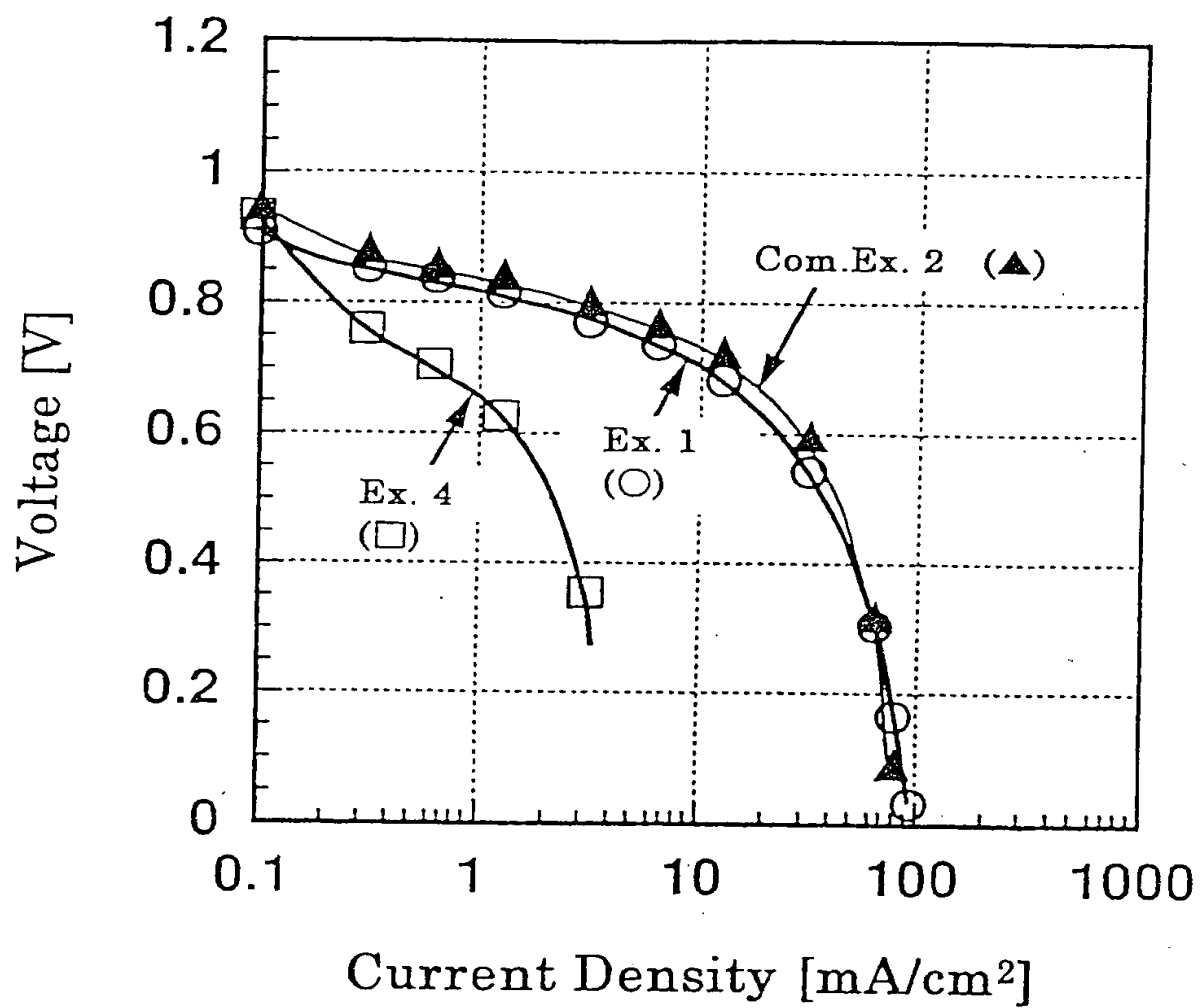
6. A method for producing a polymer electrolyte membrane for a fuel cell, which comprises forming a membrane of

the polymer electrolyte for fuel cell according to any one of claims 1 to 3 by a solution casting method, a melt pressing method or a melt extrusion method.

7. A fuel cell obtainable by using the polymer electrolyte membrane for fuel cell according to claim 5.

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Fig. 1

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 96 29752 A (DU PONT ;GROT WALTHER GUSTAV (US); RAJENDRAN GOVINDARAJULU (US)) 26 September 1996 * page 6, line 28 - page 7, line 14; claim 19 *	1,2,5-7	H01M8/10 H01M8/02 C08J5/22 C08G75/23
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 128 (C-345), 13 May 1986 & JP 60 255109 A (NITTO DENKI KOGYO KK), 16 December 1985, * abstract *	1,6	
E	DATABASE WPI Section Ch, Week 9814 Derwent Publications Ltd., London, GB; Class A26, AN 98-151029 XP002069851 & JP 10 021 943 A (SUMITOMO CHEM CO LTD) * abstract *	1-7	
X D	EP 0 029 633 A (ICI PLC) 3 June 1981 * example 1 * & JP 02 017 571 B (ICI)	1,2,4	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

H01M
C08J
C08G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	30 June 1998	Andrews, M

(54) Title: SULPHONATED POLYETHER KETONES, METHOD OF PRODUCING THEM AND THE USE THEREOF TO PRODUCE MEMBRANES

(54) Bezeichnung: SULFONIERTE POLYETHERKETONE, VERFAHREN ZU IHRER HERSTELLUNG UND VERWENDUNG ZUR HERSTELLUNG VON MEMBRANEN

(57) Abstract

The invention concerns a sulphonated aromatic polyether ketone containing units of general formula (II): [Ar-O-]$_p$-Ar-[[CO-Ar'-]$_x$-O-Ar]$_m$-[CO-Ar'-]$_y$-[O-Ar-]$_n$-CO-], in which between 1 and 100 % of the O-phenylene-CO-units are substituted with an SO$_3$M group and the sulphonated and unsulphonated O-phenylene-CO-units and the sulphonated and unsulphonated O-phenylene-O units can be in any sequence; and in which Ar, Ar', M, x, n, m, y and p have the following meanings: Ar stands for a phenylene ring with p- and/or m-bonds; Ar' stands for a phenylene, naphthylene, biphenylene-, anthrylene- or other divalent aromatic unit; x, n and m are all, independently of one another, 0 or 1; y is 0, 1, 2 or 3; p is 1, 2, 3 or 4; M stands for one or more elements selected with due consideration to ionic valencies from the following group: H, NR$_4$, in which R stands for H, C$_1$-C$_4$ alkyl, or a metal, preferably an alkali or alkaline earth metal or a metal of sub-group 8.

(57) Zusammenfassung

Sulfoniertes aromatisches Polyetherketon enthaltend Einheiten der allgemeinen Formel (II) [Ar-O-]$_p$-Ar-[[CO-Ar'-]$_x$-O-Ar]$_m$-[CO-Ar'-]$_y$-[O-Ar-]$_n$-CO-], bei dem 1 % bis 100 % der O-Phenylen-CO-Einheiten mit einer SO$_3$M-Gruppe substituiert sind und hierbei sulfonierte und unsulfonierte O-Phenylen-CO-Einheiten sowie sulfonierte und unsulfonierte O-Phenylen-O-Einheiten in beliebiger Reihenfolge zueinander stehen können, und wobei Ar, Ar', M, x, n, m, y und p folgende Bedeutung haben: Ar steht für einen Phenylenring mit p- und/oder m-Bindungen, Ar' steht für eine Phenylen-, Naphthylen-, Biphenylen-, Anthrylen- oder eine andere zweiwertige aromatische Einheit, x, n und m sind unabhängig voneinander 0 oder 1, y ist 0, 1, 2 oder 3, p ist 1, 2, 3 oder 4; M steht, unter Berücksichtigung der ionischen Wertigkeiten, für eines oder mehrere Elemente ausgewählt aus der folgenden Gruppe: H, NR$_4$, mit R=H, C$_1$-C$_4$-Alkyl-, oder ein Metall, bevorzugt ein Alkali- oder Erdalkalimetall oder ein Metall der 8. Nebengruppe.

1

SULFONIERTE POLYETHERKETONE, VERFAHREN ZU IHRER HERSTELLUNG UND VERWENDUNG ZUR HERSTELLUNG VON MEMBRANEN

Beschreibung

Die Erfindung betrifft Polymerelektrolyte, die aus einem sulfonierten aromatischen Polyetherketon bestehen, ein Verfahren zu ihrer Herstellung, Verwendung dieser Polymerelektrolyte sowie Lösungen dieser Polymerelektrolyte und Verwendung derselben.

Sulfonierte Polyetherketone stellen Kationen-Ionenaustauscher dar. Sie sind nützlich als Membranmaterialien, z.B. zur Ultrafiltration, zur Entsalzung und zur Entfernung von Mikroorganismen, da sie in vielen Fällen auch in Gegenwart von Wasser mechanisch beständig sind. Sulfonierte Polyetherketone sind protonen- und kationenleitende Materialien, die nützlich sind zur Elektrodialyse oder als Bestandteil von elektrochemischen Zellen.

Ausgangsmaterialien sind aromatische Polyetherketone wie in der allgemeinen Formel (I) angegeben,

$$[Ar\text{-}O\text{-}]_q\text{-}Ar\text{-}[[CO\text{-}Ar'\text{-}]_r\text{-}O\text{-}Ar]_s\text{-}[CO\text{-}Ar'\text{-}]_t\text{-}[O\text{-}Ar\text{-}]_u\text{-}CO\text{-}] \qquad (I)$$

wobei
Ar   einen Phenylenring mit p- und/oder m-Bindungen,
Ar'   eine Phenylen-, Naphthylen-, Biphenylen-, Anthrylen- oder eine andere zweiwertige aromatische Einheit,
r, u und s unabhängig voneinander 0 oder 1,

2

t   0,1,2 oder 3,

q   1,2,3 oder 4

bedeuten. Das Polymere mit q=1, r=0, s=1, t=0, u=0 ist unter der Bezeichnung Victrex
® im Handel verfügbar. Ebenso wird das Polymere mit q=1, r=0, s=0, t=0 und u=0 von
der Firma Victrex hergestellt. Ferner ist das Polymere mit q=1, r=0, s=0, t=2, u=1 und
Ar 1,4-Phenylen unter der Bezeichnung Ultrapek ® im Handel verfügbar.

Polyetherketone sind leicht zugänglich. Sie lassen sich prinzipiell durch eine
elektrophile Polykondensation nach Friedel-Crafts aufbauen, wobei ein
entsprechendes aromatisches Bissäuredihalogenid mit einem aromatischen Ether
umgesetzt wird. Diese Möglichkeit ist z.B. in US-3 065 205, GB-971 227, US-3 441
538, GB-1 387 303, WO 84-03 891 und in dem Aufsatz von Iwakura, Y., Uno, K. und
Tahiguchi, T.J., Polym. Sci., Pat. A-1, 6, 3345 (1968), dargestellt. Daneben kann man
die Etherketone durch nucleophile aromatische Substitution gewinnen. Hierzu wird ein
entsprechendes aromatisches Bisdiol mit einem aromatischen Bishalogenketon
umgesetzt, wie es z.B. in:R.A., Clendinning, A.G. Farnham, W.F. Hall, R.N. Johnson
and C.N. Merriam, J. Polym. Sci. A1, 5, 2375, (1967), GB-1 177 183, GB-1 141 421,
EP-0 001 879, US 4 108 837, US 4 175 175, T.E. Attwood, A.B. Newton, J.B. Rose, Br.
Polym. Journ., 4, 391, (1972); T.E. Attwood, P.C. Dawson, J.L. Freemann, L.R.J. Hoy,
J.B. Rose, P.A. Staniland, Polymer, 22, 1096, (1981) beschrieben wird.

Die Herstellung von sulfonierten Polyetherketonen aus einigen dieser Polyetherketone
wird beschrieben in EP-A-008 895, EP-A-041 780 und EP-A-575 807.

Gemäß EP-A- 008 895 wird das zu sulfonierende Polymer bei Raumtemperatur in
Schwefelsäure von 98 Gew.-% suspendiert. Der Löseprozeß und die Sulfonierung
laufen gleichzeitig ab, wobei allmählich eine sehr viskose Lösung erhalten wird. Diese
Lösung wird entweder sich selbst überlassen oder bei gleicher Temperatur mit
Schwefelsäure gleicher Konzentration verdünnt. Die Reaktion verläuft sehr langsam.
Nach 10 Wochen waren erst ca. 90 % der sulfonierbaren Phenylen-Einheiten

3

sulfoniert. In den eingesetzten Polyetherketonen betrug das Zahlenverhältnis von
Etherbrücken zu CO-Brücken etwa 2:1. Gemäß EP-A-008 895 werden unter diesen
Bedingungen nur O-Phenylen-O-Einheiten sulfoniert.

Nach dem Verfahren gemäß EP-A- 041 780 werden bei erhöhter Temperatur
aromatische Polyetherketone, die Copolymere darstellen, sulfoniert. Nur ein Teil der
Monomereinheiten (A) ist der Sulfonierung zugänglich, während andere
Monomereinheiten (B) nicht sulfoniert werden. Durch das Verhältnis A/B läßt sich so
der Sulfonierungsgrad steuern. Jedoch bleiben auch hier die Reaktionsbedingungen
während des Löseprozesses und danach unverändert. Entsprechende Homopolymere
(A) würden unter den angegebenen Bedingungen zu hoch sulfoniert sein und damit zu
wasserlöslichen Verbindungen führen. Da hier die Sulfonierung bereits während des
Auflöseprozesses des Polymeren stattfindet, ist es schwierig, den Sulfonierungsgrad
zu kontrollieren und niedrig sulfonierte Produkte zu erhalten. Bei dem Verfahren
gemäß EP-A-041 780 werden unter diesen Bedingungen ebenfalls nur
O-Phenylen-O-Einheiten sulfoniert.

Bei dem in EP-A-575 807 offenbarten Verfahren wird das zu sulfonierende Polymer bei
Raumtemperatur in Schwefelsäure von 94 bis 97 Gew.-% suspendiert. Der Löseprozeß
und eine teilweise Sulfonierung des Polymers laufen gleichzeitig ab, wobei allmählich
eine viskose Lösung erhalten wird. Die Lösung wird mit einem sulfonierenden Agens
versetzt bis die Schwefelsäurekonzentration 98 bis 99,9 Gew.-% beträgt. Die Lösung
verbleibt bis der gewünschte Sulfonierungsgrad erreicht ist und wird dann
aufgearbeitet. Unter diesen Bedingungen werden nur O-Phenylen-O-Einheiten
sulfoniert, während O-Phenylen-CO-Einheiten nicht angegriffen werden. Dies wird auch
von Daoust et al. (Polymer, Vol. 35 (25), 5491-5497 (1994)) bestätigt, wobei der
Sulfonierungsprozeß beschränkt ist auf eine Sulfonsäuregruppe pro
Wiederholungseinheit und auf eine der vier äquivalenten Positionen des von zwei
Ethereinheiten umgebenen Phenylenrings. Die anderen beiden Phenylenringe werden

nach Daoust von der benachbarten Ketoneinheit so stark desaktiviert, daß hier keine Sulfonierung stattfindet.

Bei der Sulfonierung von Polyetherketonen unter Verwendung von Chlorsulfonsäure oder einem SO3/Triethylphosphat-Komplex wird ein hoher Grad an Vernetzung sowie Zersetzung der Polymerhauptkette beobachtet (Marvel et al., Journal of Polymer Science, Polymer Chem. Edition, vol. 23, 2205-2223, (1985) und Bishop et. al., Macromolecules, vol. 18, 86-93 (1985)).

Bei den im Stand der Technik bekannten Verfahren werden von den eingesetzten Polyetherketonen nur O-Phenylen-O-Einheiten sulfoniert, während O-Phenylen-CO-Einheiten und CO-Phenylen-CO-Einheiten nicht oder nur zu einem verschwindend geringen Anteil sulfoniert werden oder bei Anwendung drastischerer Bedingungen erfolgt Vernetzung oder eine Zerstörung der Polymerhauptkette. Polymere, die keine O-Phenylen-O-Einheiten aufweisen, lassen sich nicht in signifikantem Umfang sulfonieren. Die bei Anwendung härterer Reaktionsbedingungen erhaltenen Produkte sind in den herkömmlichen Lösemitteln unlöslich und können daher über Lösung nicht oder nur sehr schwer weiterverarbeitet werden.

Nach dem Stand der Technik war nicht zu erwarten, daß sich O-Phenylen-CO-Einheiten in einem Polyetherketon sulfonieren lassen. Ebenfalls war nach dem Stand der Technik nicht zu erwarten, daß sich entsprechend sulfonierte Produkte in herkömmlichen Lösemitteln lösen lassen. Nach dem Stand der Technik galt es als unmöglich, schonend in einem Polyetherketon Phenylenringe zu sulfonieren, die einer Ketogruppe direkt benachbart sind, wenn nicht gleichzeitig Vernetzung oder Abbau der Polymerhauptkette eintritt.

Die Aufgabe der vorliegenden Erfindung ist es somit, ein schonendes und kontrollierbares Verfahren zur Sulfonierung von Polyetherketonen der allgemeinen Formel (I) bereitzustellen, wobei sich mit diesem Verfahren neben

O-Phenylen-O-Einheiten auch O-Phenylen-CO-Einheiten sulfonieren lassen und auf diese Weise neue sulfonierte Polyetherketone zu gewinnen. Weitere Aufgabe ist es, Lösungen dieser Polymere herzustellen.

Überraschenderweise wurde nun gefunden, daß sich erfindungsgemäße Polymere gut und kontrollierbar neben den O-Phenylen-O-Einheiten auch an O-Phenylen-CO-Einheiten sulfonieren lassen, wobei die erhaltenen Produkte ab einem gewissen Sulfonierungsgrad sogar löslich sind. Sogar Polymere, die nur O-Phenylen-CO-Einheiten enthalten, sind einer gezielten Sulfonierung zugänglich.

Die vorliegende Erfindung betrifft daher ein sulfoniertes aromatisches Polyetherketon enthaltend Einheiten der allgemeinen Formel (II)

$$[[Ar-O-]_p-Ar-[[CO-Ar'-]_x-O-Ar]_m-[CO-Ar'-]_y-[O-Ar-]_n-CO-] \qquad (II)$$

bei denen 1 % bis 100 % der O-Phenylen-CO-Einheiten mit einer SO_3M-Gruppe substituiert sind und hierbei sulfonierte und unsulfonierte O-Phenylen-CO-Einheiten sowie sulfonierte und unsulfonierte O-Phenylen-O-Einheiten in beliebiger Reihenfolge zueinander stehen können

und wobei Ar, Ar', M, x, n, m, y und p folgende Bedeutung haben:

Ar   steht für einen Phenylenring mit p- und/oder m-Bindungen,

Ar'   steht für eine Phenylen-, Naphthylen-, Biphenylen-, Anthrylen- oder eine andere zweiwertige aromatische Einheit,

x, n und m sind unabhängig voneinander 0 oder 1,

y   ist 0,1,2 oder 3,

p   ist 1,2,3 oder 4 und

M steht, unter Berücksichtigung der ionischen Wertigkeiten, für eines oder mehrere Elemente ausgewählt aus der folgenden Gruppe: H, NR_4^+, mit R= H, C_1-C_4-Alkyl-, oder

ein Alkali- oder Erdalkalimetall oder ein Metall der 8. Nebengruppe, vorzugsweise für H, NR_4^+, Na, K, Ca, Mg, Fe und Pt.

Ebenso betrifft die vorliegende Erfindung ein Verfahren zur Herstellung dieser sulfonierten Polyetherketone mit Einheiten der allgemeinen Formel (II), Polymerelektrolytlösungen enthaltend die genannten Polymere sowie die Verwendung derartiger Polymerelektrolytlösungen.

Mit Hilfe des erfindungsgemäßen Verfahrens können aromatische Polyetherketone mit Einheiten der allgemeinen Formel (I) auch an den O-Phenylen-CO-Einheiten sulfoniert werden.

In Übereinstimmung mit der veröffentlichten Literatur wird gefunden, daß die Sulfonierung bevorzugt an den O-Phenylen-O-Einheiten der Polyetherketone stattfindet. Überraschenderweise wurde gefunden, daß mit Hilfe des erfindungsgemäßen Verfahrens bei höheren Sulfonierungsgraden auch ein signifikanter Anteil der O-Phenylen-CO-Einheiten sulfoniert wird.

Das Verfahren ist dadurch gekennzeichnet, daß man das aromatische Polyetherketon in Schwefelsäure von 94 bis 98 Gew.-% löst, man die erhaltenen Lösung mit einem sulfonierenden Agens versetzt, bis die Schwefelsäurekonzentration 98 bis 100 Gew.-% oder bis die Oleumkonzentration 0,01 bis 15 Gew.-% SO_3 beträgt, man eine geeignete Reaktionstemperatur einstellt und man den Reaktionsansatz aufarbeitet, sobald der gewünschte Sulfonierungsgrad erreicht ist.

Vorzugsweise wird das aromatische Polyetherketon in Schwefelsäure unter schonenden Bedingungen gelöst, d.h. unter Bedingungen, bei denen eine Sulfonierung weitgehend unterdrückt wird, bzw. es noch nicht zu einer Sulfonierung kommt. Vorzugsweise beträgt die Konzentration der zum Auflösen verwendeten Schwefelsäure 94 bis 97 Gew.-%. Die Lösetemperatur wird so niedrig wie möglich gewählt, um ein

Einsetzen der Sulfonierungsreaktion in diesem Stadium weitgehend zu vermeiden. Im allgemeinen liegt die Lösetemperatur zwischen 10 und 80°C, insbesondere zwischen 20 und 70°C, vorzugsweise zwischen 30 bis 60°C.

Insbesondere stehen sämtliche zweiwertigen aromatischen Reste Ar und Ar' des zu sulfonierenden Polymers für Phenylen, vorzugsweise für 1,4-Phenylen.

Bevorzugt werden Homopolymere der allgemeinen Formeln (III), (IV) und (V) eingesetzt, so daß das resultierende, erfindungsgemäße Polyetherketon sulfonierte Einheiten dieser Formeln enthält. Das beschriebene Sulfonierungsverfahren erlaubt unter kontrollierten Bedingungen die Sulfonierung von Polyetherketonen auch an O-Phenylen-CO-Einheiten.

(I I I)

(I V)

(V)

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In einer weiteren bevorzugten Ausführungsform ist das zu sulfonierende Polyetherketon ein Copolymer enthaltend mindestens zwei verschiedenen Einheiten der Formeln (II), (III), (IV), (V) und (VI).

(VI)

Für das Homopolymer der Formel (III) werden beispielsweise nach einem Lösevorgang bei maximal 80°C und nach 5 h bei Raumtemperatur in Schwefelsäure von 95 oder 97 Gew.-% Sulfonierungsgrade von weniger als 14 mol-% bezogen auf eine Wiederholeinheit beobachtet.

Für das Homopolymer der Formel (IV) werden z.B. nach einem Lösevorgang bei maximal 80°C und nach 24 h bei Raumtemperatur in Schwefelsäure von 95 oder 97 Gew.-% und bei einer Sulfonierungstemperatur im Bereich von 30 bis 90°C Sulfonierungsgrade von ca. 25 mol-% bezogen auf eine Wiederholeinheit beobachtet.

Für das Homopolymer der Formel (V) wird z.B. nach einem Lösevorgang bei 80°C und nach 24 h bei Raumtemperatur in Schwefelsäure von 95 oder 97Gew.% ein Sulfonierungsgrad von 12 mol% bezogen auf eine Wiederholungseinheit beobachtet. Die Sulfonierungstemperatur liegt vorzugsweise im Bereich von 50 bis 100°C.

Bevorzugt sind Lösebedingungen, die zu einem Sulfonierungsgrad von maximal 35 mol-% bezogen auf eine Wiederholeinheit führen. Während des Lösevorgangs ist eine

Sulfonierung der Hauptkette weitgehend unterdrückt. Untersuchungen haben gezeigt, daß während des Lösevorgangs kein Abbau eintritt.

Als sulfonierendes Agens, das zur Erhöhung der Schwefelsäure-Konzentration und zur Sulfonierung dient, werden vorzugsweise Schwefelsäure, rauchende Schwefelsäure, Oleum, Chlorsulfonsäure und Schwefeltrioxid eingesetzt.

In Abhängigkeit von dem Verhältnis der O-Phenylen-O-Einheiten zu den O-Phenylen-CO-Einheiten zu den CO-Phenylen-CO-Einheiten und in Abhängigkeit von der Abfolge dieser Einheiten entlang der Polymerhauptkette ändert sich das Sulfonierungsverhalten der Polyetherketone. Änderungen im Elektronenhaushalt der Phenylenringe beeinflussen direkt deren Sulfonierungsverhalten. Aber auch Nebenreaktionen werden durch Änderungen im Elektronenhaushalt der Phenylenringe beeinflußt: Die Kombination der Reaktionsparameter, der Schwefelsäurekonzentration, der Reaktionstemperatur und der Reaktionsdauer, bestimmt in welchem Maße O-Phenylen-O-Einheiten und O-Phenylen-CO-Einheiten sulfoniert werden und in welchem Maß Vernetzung über Sulfongruppen oder Hauptkettenabbau auftreten.

Für jedes Polyetherketon sind daher andere Kombinationen der Reaktionsparameter ideal, um einerseits einen hohen Anteil an sulfonierten O-Phenylen-CO-Einheiten zu erhalten und um andererseits Vernetzungsreaktionen und Kettenabbau auf einem möglichst geringen Niveau zu halten. Das erfindungsgemäße Verfahren zeichnet sich dadurch aus, daß man die geeignete Parameterkombination auswählt, um in diesem Sinne einen möglichst günstigen Verlauf der Sulfonierungsreaktion zu gewährleisten.

Im allgemeinen gilt, daß elektronenreiche aromatische Strukturen bevorzugt sulfoniert werden. Sind verschiedene Reaktionsorte für die Sulfonierung vorhanden, d.h. weist das Eduktpolymer verschiedene aromatische Strukturen mit unterschiedlichen Elektronendichten auf, so hängt die Selektivität des Reaktionsortes unter anderem von den jeweiligen Reaktionsparametern (Zeit, Temperatur, Säurekonzentration) ab.

Um einen bevorzugten Sulfonierungsgrad in O-Phenylen-CO-Einheiten zu erreichen, sind je nach Struktur des Eduktpolymers verschiedene Selektivitäten erwünscht. Daher sind abhängig von der Struktur des Eduktpolymers unterschiedliche Kombinationen an Reaktionsparametern besonders bevorzugt.

Die Polyetherketone werden dazu entsprechend des Elektronenreichtums ihrer aromatischen Strukturen unterteilt.
O-Phenylen-O-Einheiten sind elektronenreicher und daher leichter zu sulfonieren als O-Phenylen-CO-Einheiten, während O-Phenylen-CO-Einheiten wiederum leichter sulfonierbar sind als CO-Phenylen-CO-Einheiten.
Als Maß für die Sulfonierbarkeit (S) eines Polyetherketons gilt:

$$S = 4\ EE + EK - KK$$

wobei

S= Maßzahl für die Sulfonierbarkeit

EE= prozentualer Anteil der O-Phenylen-O-Einheiten

EK= prozentualer Anteil der O-Phenylen-CO-Einheiten

KK= prozentualer Anteil der CO-Phenylen-CO-Einheiten an den aromatischen Strukturen im Polymer.

Damit gilt:

$$EE + EK + KK = 100\%$$

Für die Auswahl der bevorzugten Kombinationen von Reaktionsparametern muß ebenfalls das Verhältnis V berücksichtigt werden:

$$V = EK\ /\ EE$$

Allgemein kann man davon ausgehen, daß

1.   je höher V ist, desto drastischere Reaktionsbedingungen sind notwendig, um einen hohen Anteil an sulfonierten O-Phenylen-CO-Einheiten zu erhalten;

2.   je geringer die Sulfonierbarkeit S, desto längere Zeiten und/oder härtere Reaktionsbedingungen sind notwendig, um den gewünschten Sulfonierungsgrad zu erzielen;

3.   je härter die Reaktionsbedingungen und je länger die Reaktionszeiten, desto mehr Nebenreaktionen treten auf.

Unterteilt man die zu sulfonierenden Polymere nach dem oben aufgeführten Schema, so ergibt sich folgende Einteilung: Polymere mit S > 150 % gelten als leicht sulfonierbar, Polymere mit 150% > S > 80% sind mäßig sulfonierbar und Polymere mit S < 80% werden als schwer sulfonierbar eingestuft.

Berücksichtigt man diese Punkte, so zeigt sich, daß bestimmte Kombinationen an Reaktionsparametern besonders geeignet sind, die gewünschten Sulfonierungsprodukte herzustellen. Andere Kombinationen führen nicht zu den gewünschten Produkten. Die Beispiele in den Tabellen verdeutlichen diese Abhängigkeit.

Betrachtet man beispielsweise ein mäßig sulfonierbares Polyetherketon der Formel (III) (Tabelle 1), so zeigt sich, daß der Anteil der sulfonierten O-Phenylen-CO-Einheiten bei gleichbleibender Temperatur mit zunehmender Reaktionszeit zunimmt. Hierbei ist es möglich, die Temperatur so einzustellen, daß die Sulfonierung von O-Phenylen-CO-Einheiten in einstellbaren Zeiträumen erfolgt und gleichzeitig eventuelle unerwünschte Nebenreaktionen weitgehend ausgeschlossen werden. Unterhalb einer gewissen Temperaturschwelle (60°C) beobachtet man jedoch auch bei längeren Reaktionszeiten keine oder nur eine minimale Sulfonierung der Ether-Keton-Einheiten.

Das gleiche gilt für die Reaktionskonzentration der Schwefelsäure. So wird bei einer Schwefelsäurekonzentration von $\leq$ 90 Gew.%, auch bei entsprechend langen

Reaktionszeiten, keine Sulfonierung der O-Phenylen-CO-Einheiten beobachtet.

Bei einer Säurekonzentration von >90 ≤ 99 Gew.% beobachtet man dagegen schon bei mäßigen Temperaturen und kurzen Reaktionszeiten eine merkliche Sulfonierung, die mit zunehmender Reaktionszeit, unter Beibehaltung der Temperatur, noch gesteigert werden kann.

Durch eine geeignete Kombination der Reaktionsparameter gelangt man mit Hilfe des erfindungsgemäßen Verfahrens unter milden Bedingungen zu Polymeren mit einer hohen Sulfonierung der Ether-Keton-Einheiten (1 bis 50 %), wobei störende Nebenreaktion weitgehend unterdrückt werden. Durch eine geeignete Kombination der Reaktionsparameter gelangt man mit Hilfe des erfindungsgemäßen Verfahrens unter härteren Bedingungen zu Polymeren mit einer hohen Sulfonierung der Ether-Keton-Einheiten (1 bis 100 %).

Bei der Herstellung der erfindungsgemäßen sulfonierten Polymere wird die Konzentration der Schwefelsäure nach dem Lösevorgang, z.B. durch Zugabe von Oleum, erhöht bis die Schwefelsäurekonzentration 98 bis 100 Gew.-% oder bis die Oleumkonzentration 0,01 bis 15 Gew.-% SO_3 beträgt, insbesondere bis die Schwefelsäurekonzentration 98,5 bis 100 Gew.-% oder bis die Oleumkonzentration 0,01 bis 5 Gew.-% SO_3 beträgt, vorzugsweise bis die Schwefelsäurekonzentration 98,5 bis 100 Gew.-% oder bis die Oleumkonzentration 0,01 bis 1 Gew.-% SO_3 beträgt.

Die Reaktionstemperatur bei der eigentlichen Sulfonierung kann höher oder auch niedriger liegen als beim Löseprozeß. Im allgemeinen sulfoniert man bei Temperaturen im Bereich von 10 bis 100°C, insbesondere 30 bis 95°C, besonders bevorzugt 50 bis 90°C. Sowohl eine Temperaturerhöhung als auch eine Verlängerung der Reaktionszeit bewirken eine Erhöhung des Sulfonierungsgrads des Polymers. Insbesondere beträgt die Temperatur der Lösung nach Zugabe des sulfonierenden Agens mindestens 30°C. Typische Reaktionszeiten liegen im Bereich von 45 Minuten bis 24 Stunden, vorzugsweise 1 und 8 Stunden, besonders bevorzugt im Bereich von 1 bis 4 Stunden.

Sobald der gewünschte Sulfonierungsgrad erreicht ist, wird die Reaktion abgebrochen und das Polymer z.B. im wäßrigen Milieu ausgefällt, isoliert und getrocknet.

Untersuchungen haben gezeigt, daß während der Sulfonierungsreaktion nur in geringem Maße ein Abbau der Polymerhauptkette eintritt. Gegebenenfalls vorhandene CO-Phenylen-CO-Einheiten des eingesetzten aromatischen Polyetherketons werden nach dem erfindungsgemäßen Verfahren nicht sulfoniert.

Der Vorteil der sulfonierten O-Phenylen-CO-Einheiten im Vergleich zu sulfonierten O-Phenylen-O-Einheiten in herkömmlichen Polymeren liegt unter anderem in der besseren hydrolytischen Stabilität der SO_3H- bzw. der SO_3M-Gruppen. In wäßriger Umgebung und bei erhöhten Temperaturen kann Desulfonierung der sulfonierten Polyetherketone auftreten. Es ist bekannt, daß das Maß der hydrolytischen Desulfonierung von dem Elektronenreichtum der aromatischen Ringe abhängt. Beim Einsatz von sulfonierten Polymeren im wäßrigen Medium ist es unabdingbar, daß die Eigenschaften des sulfonierten Polymers konstant bleiben. Bei solchen Anwendungen ist es daher vorteilhaft ein sulfoniertes Polyetherketon zu verwenden, das Desulfonierung nicht oder nur zu einem geringem Umfang zuläßt. Ein Polymer, dessen Sulfonsäuregruppen zu einem möglichst hohem Grade an O-Phenylen-CO-Einheiten lokalisiert sind, ist demnach in solchen Fällen insbesondere geeignet. Die Sulfonsäuregruppen (SO_3H) können nach der Sulfonierung mit den bekannten Verfahren in ihre Salzform (SO_3M) überführt werden.

Das beschriebene Verfahren ergibt Sulfonierungsprodukte, die sich ab einem bestimmten Sulfonierungsgrad in herkömmlichen Lösemitteln, wie z.B. NMP oder DMSO, lösen lassen. Die auf diese Weise hergestellten Polymerelektrolytlösungen enthalten in einer bevorzugten Ausführungsform mindestens 1 Gew.% Polyetherketone der Formel (II) und als Hauptbestandteil aprotische dipolare Lösemittel, wie z.B. N-Methylpyrrolidon (NMP) oder Dimethylsulfoxid (DMSO).
Je nach weiterem Verwendungszweck der Polymerelektrolytlösung kann diese

gegebenenfalls ein weiteres unsulfoniertes Polymer oder auch geringe Anteile von Hilfsstoffen enthalten.

Die erfindungsgemäßen Polymerelektrolytlösungen eignen sich insbesondere zur Herstellung von asymmetrischen Membranen, zum Beispiel für die Nano-, Ultra- oder Mikrofiltration sowie zur Herstellung von dichten Filmen mit einer Dicke im Bereich von 5 μm bis 1 mm.

Eine besonders wichtige Rolle kommt den erfindungsgemäßen Polymerelektrolytlösungen bei der Herstellung eines besonders intensiven Kontaktes zwischen zwei Polymerelektrolytoberflächen zu. Eine poröse oder rauhe Oberfläche kann so z.B. nach Kontaktieren der Lösung mit einem Fällungsmittel erzielt werden.

Die erfindungsgemäßen Polymere sowie Polymerelektrolytlösungen oder Polymerfilme enthaltend diese Polymere eignen sich insbesondere zur Verwendung in elektrochemischen Zellen, beispielsweise Brennstoffzellen oder Wasserelektrolysezellen.

Beispiele:

In einer Vierhals-Rührapparatur mit Tropftrichter und Ölbad wurde 96%ige konzentrierte Schwefelsäure vorgelegt und verschiedene Polyetherketone der allgemeinen Formel (I) gelöst. Danach wurde Oleum (Gehalt 20 Gew.-% SO_3) zutitriert, bis ein sulfonierendes Gemisch erreicht wurde mit Schwefelsäurekonzentrationen von 98,5 bis 100 Gew.-% oder Oleumkonzentrationen von 0,1 bis 0,7 Gew.-% SO_3. Anschließend wurden die Mischung auf Reaktionstemperatur gebracht, um eine optimale und kontrollierte Sulfonierung zu gewährleisten. Nach Erreichen des gewünschten Sulfonierungsgrades wurde die Reaktion gestoppt und das Produkt

isoliert. Die Charakterisierung des Produktes erfolgt mittels Viskosimetrie, ^{13}C-NMR-Spektroskopie und Elementaranalyse.

Die Versuche in Tabelle 1 wurden mit einem Homopolymeren der allgemeinen Formel (III) durchgeführt. Die Versuche in Tabelle 2 wurden mit einem Homopolymeren der allgemeinen Formel (IV) durchgeführt. Polymere der Formel (III) besitzen einen S-Wert von 125 % und sind daher als mäßig sulfonierbar einzustufen, die der Formel (IV) besitzen einen S-Wert von 180 % und gelten erfindungsgemäß als leicht sulfonierbar.

Beispiele, die einen Sulfonierungsgrad der O-Phenylen-CO-Einheiten (SEK bezogen auf eine Wiederholungseinheit in mol%) von Null aufweisen sind als Vergleichsbeispiele anzusehen.

In den Tabellen werden folgende Abkürzungen benutzt:

NR   Versuchsnummer

LT   Lösetemperatur in °C

LZ   Lösezeit in Minuten

PK   Polymerkonzentration in Gew.-%

RK   Reaktionskonzentration von Oleum in Gew.-% SO_3

RC   Reaktionskonzentration von Schwefelsäure in Gew.-% H_2SO_4

RT   Reaktionstemperatur in °C (Sulfonierungstemperatur)

RZ   Reaktionszeit in Minuten

SG   Sulfonierungsgrad in mol-% bezogen auf eine Wiederholungseinheit

SEE   Sulfonierungsgrad der O-Phenylen-O-Einheiten in mol-% bezogen auf eine Wiederholungseinheit

SEK   Sulfonierungsgrad der O-Phenylen-CO-Einheiten in mol-% bezogen auf eine Wiederholungseinheit

IV   inhärente Viskosität in dl/g (gemessen in konz. H_2SO_4 bei 25°C)

Tabelle 1:

Homopolymer der Formel (III)

Nr.	PK	LT	LZ	RC	RT	RZ	SG	SEE	SEK	IV
1	6,7	60	60	98,5	80	0	32,3	31,0	1,3	0,86
2	6,7	60	60	98,5	80	30	53,1	47,8	5,3	0,84
3	6,7	60	60	98,5	80	60	71	62,9	8,1	0,84
4	6,7	60	60	98,5	80	90	82,7	73,4	9,3	0,80
5	6,7	60	60	98,5	80	120	88,5	49,3	9,2	0,80
6	6,7	60	60	98,5	80	150	94,0	83,9	10,1	0,76
7	6,7	60	60	98,5	80	210	100,6	90,0	10,6	C,73
8	6,7	60	60	98,5	80	240	102,1	92,1	10,0	0,72
9	6,7	60	60	98,5	60	0	29,0	29,0	0	0,87
10	6,7	60	60	98,5	60	30	33,7	33,7	0	0,87
11	6,7	60	60	98,5	60	60	38,8	38,8	0	0,86
12	6,7	60	60	98,5	60	90	42,3	42,3	0	0,84
13	6,7	60	60	98,5	60	120	44,9	44,9	0	0,81
14	6,7	60	60	98,5	60	150	48,2	48,2	0	0,79
15	6,7	60	60	98,5	60	210	53,1	53,1	0	0,77
16	6,7	60	60	98,5	60	240	55,8	54,8	1,0	0,72
17	6,7	60	60	98,5	90	0	20,5	20,5	0	0,83
18	6,7	60	60	98,5	90	30	33,1	30,8	2,3	0,82
19	6,7	60	60	98,5	90	60	48,0	43,2	4,8	0,79
20	6,7	60	60	98,5	90	90	58,4	51,6	6,8	0,74
21	6,7	60	60	98,5	90	120	66,7	58,1	8,6	0,70
22	6,7	60	60	98,5	90	150	74,6	65,0	9,6	0,65
23	6,7	60	60	98,5	90	210	85,7	73,9	11,8	0,61
24	6,7	60	60	98,5	90	240	90,0	77,0	13,0	0,59
25	6,7	60	60	98,5	100	0	19,5	19,5	0	0,80
26	6,7	60	60	98,5	100	30	43,4	39,1	4,3	0,78
27	6,7	60	60	98,5	100	60	74,3	64,7	9,6	0,74

28	6,7	60	60	98,5	100	90	87,7	72,8	14,9	0,71
29	6,7	60	60	98,5	100	120	96,5	83,0	13,5	0,68
30	6,7	60	60	98,5	100	150	103,2	86,7	16,5	0,63
31	6,7	60	60	98,5	100	210	11,8	93,5	18,3	0,59
32	6,7	60	60	98,5	100	240	115,2	95,3	19,9	0,55
33	6,7	60	60	90,0	80	0	37,7	37,7	0	0,86
34	6,7	60	60	90,0	80	30	38,2	38,2	0	0,86
35	6,7	60	60	90,0	80	60	38,7	38,7	0	0,83
36	6,7	60	60	90,0	80	90	39,2	39,2	0	0,82
37	6,7	60	60	90,0	80	120	39,7	39,7	0	0,81
38	6,7	60	60	90,0	80	150	41,6	41,6	0	0,79
39	6,7	60	60	90,0	80	210	44,3	44,3	0	0,76
40	6,7	60	60	90,0	80	240	45,7	45,7	0	0,75
41	6,7	60	60	99,0	80	0	30,4	29,4	1,0	0,85
42	6,7	60	60	99,0	80	30	48,2	43,3	4,9	0,84
43	6,7	60	60	99,0	80	60	68,3	59,9	8,4	0,81
44	6,7	60	60	99,0	80	90	82,0	73,9	8,1	0,79
45	6,7	60	60	99,0	80	120	88,9	76,1	12,8	0,77
46	6,7	60	60	99,0	80	150	93,9	83,0	10,9	0,73
47	6,7	60	60	99,0	80	210	99,5	84,6	14,9	0,70
48	6,7	60	60	99,0	80	240	101,8	86,5	15,3	0,68
49	6,7	60	60	95,2	80	0	25,4	25,4	0	0,85
50	6,7	60	60	95,2	80	30	29,4	29,4	0	0,85
51	6,7	60	60	95,2	80	60	32,8	32,8	0	0,85
52	6,7	60	60	95,2	80	90	35,4	35,4	0	0,84
53	6,7	60	60	95,2	80	120	38,2	38,2	0	0,84
54	6,7	60	60	95,2	80	150	41,0	41	0	0,80
55	6,7	60	60	95,2	80	210	45,1	46,1	0	0,78
56	6,7	60	60	95,2	80	240	48,4	48,4	0	0,76

Tabelle 2:

Homopolymer der Formel (IV)

Nr.	PK	LT	LZ	RC	RT	RZ	SG	SEE	SEK	IV
1	6,7	60	60	95	60	0	27,2	27,2	0	0,93
2	6,7	60	60	95	60	30	32,4	32,4	0	0,93
3	6,7	60	60	95	60	60	35,7	35,7	0	0,92
4	6,7	60	60	95	60	90	39,1	39,1	0	0,90
5	6,7	60	60	95	60	120	42,5	42,5	0	0,87
6	6,7	60	60	95	60	180	49,3	49,3	0	0,86
7	6,7	60	60	95	60	240	54,8	54,0	0,8	0,86
8	6,7	60	60	95	60	300	59,1	58,1	1,0	0,85
9	6,7	60	60	95	60	360	63,6	62,5	1,1	0,85
10	6,7	60	60	97	70	0	34,3	33,0	1,3	0,88
11	6,7	60	60	97	70	30	59,7	53,2	6,5	0,87
12	6,7	60	60	97	70	60	72,1	63,8	8,3	0,86
13	6,7	60	60	97	70	90	82,2	72,7	9,5	0,84
14	6,7	60	60	97	70	120	89,4	79,9	9,5	0,82
15	6,7	60	60	97	70	150	101,5	89,3	12,2	0,79
16	6,7	60	60	97	70	180	110,2	96,2	14,0	0,75
17	6,7	60	60	97	70	240	116,3	100	16,3	0,74
18	6,7	60	60	97	70	300	122,7	100	22,7	0,73
19	6,7	60	60	98	90	0	31,2	29,1	1,1	0,84
20	6,7	60	60	98	90	30	103,9	89,5	14,4	0,80
21	6,7	60	60	98	90	60	119,8	97,8	22,0	0,78
22	6,7	60	60	98	90	90	128,5	100	28,5	0,72
23	6,7	60	60	98	90	120	140,2	100	40,2	0,70
24	6,7	60	60	98	90	150	145,2	100	45,2	0,68
25	6,7	60	60	98	90	225	148,7	100	48,7	0,65
26	6,7	60	60	98	60	0	32,5	31,7	0,8	0,87
27	6,7	60	60	98	60	30	55,4	49,9	5,5	0,87

Nr.	PK	LT	LZ	RC	RT	RZ	SG	SEE	SEK	IV
28	6,7	60	60	98	60	60	68,1	60,5	7,6	0,86
29	6,7	60	60	98	60	90	79,5	72,6	6,9	0,84
30	6,7	60	60	98	60	120	89,2	80,8	8,4	0,83
31	6,7	60	60	98	60	150	96,5	86,5	10,0	0,78
32	6,7	60	60	98	60	180	102,1	93,9	8,2	0,75
33	6,7	60	60	98	60	240	110,6	96,5	14,1	0,72
34	6,7	60	60	98	60	300	121,8	100	21,8	0,70
35	6,7	60	60	95	90	0	35,5	35,5	0	0,85
36	6,7	60	60	95	90	30	58,2	50,1	8,1	0,85
37	6,7	60	60	95	90	60	82,3	73,4	8,9	0,84
38	6,7	60	60	95	90	90	95,7	86,5	9,2	0,81
39	6,7	60	60	95	90	120	105,1	97,6	7,5	0,79
40	6,7	60	60	95	90	150	115,3	98,5	16,8	0,76
41	6,7	60	60	95	90	180	120,7	100	20,7	0,76
42	6,7	60	60	95	90	240	132,4	100	32,4	0,73
43	6,7	60	60	95	90	300	135,8	100	35,8	0,72

Tabelle 3:

Homopolymere der Formel (V)

NR.	PK	LT	LZ	RK	RT	RZ	SEE	SEK	SG	IV
1	6,7	50	60	0,4	60	0	0	2,3	2,3	0,92
2	6,7	50	60	0,4	60	30	0	8,7	8,7	0,91
3	6,7	50	60	0,4	60	60	0	14,0	14,0	0,88
4	6,7	50	60	0,4	60	90	0	17,2	17,2	0,84
5	6,7	50	60	0,4	60	120	0	20,2	20,2	0,85
6	6,7	50	60	0,4	60	150	0	23,5	23,5	0,81
7	6,7	50	60	0,7	50	0	0	3,7	3,7	1,00
8	6,7	50	60	0,7	50	30	0	7,0	7,0	0,97
9	6,7	50	60	0,7	50	60	0	11,1	11,1	0,92
10	6,7	50	60	0,7	50	120	0	17,8	17,8	0,90
11	6,7	50	60	0,7	50	180	0	22,1	22,1	0,88
12	6,7	50	60	0,7	50	240	0	26,0	26,0	0,85
13	6,7	50	60	0,7	50	360	0	31,5	31,5	0,82
14	6,7	50	60	0,7	50	460	0	38,2	38,2	0,75
15	6,7	50	60	0,7	50	525	0	41,0	41,0	0,73
16	6,7	50	60	0,7	70	0	0	2,7	2,7	0,95
17	6,7	50	60	0,7	70	60	0	40,2	40,2	0,78
18	6,7	50	60	0,7	70	120	0	62,3	62,3	0,72
19	6,7	50	60	0,7	70	180	0	75,2	75,2	0,61
20	6,7	50	60	0,7	70	240	0	84,2	84,2	0,59
21	6,7	50	60	0,7	70	320	0	92,0	92,0	0,56
22	6,7	50	60	0,1	50	0	0	1,2	1,2	1,03
23	6,7	50	60	0,1	50	60	0	2,1	2,1	0,98
24	6,7	50	60	0,1	50	120	0	4,1	4,1	0,93
25	6,7	50	60	0,1	50	180	0	5,7	5,7	0,90

NR	PK	LT	LZ	RK	RT	RZ	SEE	SEK	SG	IV
26	6,7	50	60	0,1	50	240	0	7,3	7,3	0,88
27	6,7	50	60	0,1	50	300	0	9,1	9,1	0,89
28	6,7	50	60	0,1	50	435	0	12,9	12,9	0,85
29	6,7	50	60	0,1	70	0	0	2,5	2,5	0,90
30	6,7	50	60	0,1	70	30	0	14,9	14,9	0,88
31	6,7	50	60	0,1	70	60	0	17,7	17,7	0,86
32	6,7	50	60	0,1	70	120	0	21,2	21,2	0,83
33	6,7	50	60	0,1	70	180	0	23,4	23,4	0,78
34	6,7	50	60	0,1	70	330	0	31,9	31,9	0,73
35	6,7	50	60	0,1	70	390	0	35,2	35,2	0,71

Patentansprüche:

1. Sulfoniertes aromatisches Polyetherketon enthaltend Einheiten der allgemeinen
    Formel (II)

    $[Ar-O-]_p-Ar-[[CO-Ar'-]_x-O-Ar]_m-[CO-Ar'-]_y-[O-Ar-]_n-CO-]$ (II)

    bei dem 1 % bis 100 % der O-Phenylen-CO-Einheiten mit einer SO_3M-Gruppe
    substituiert sind und hierbei sulfonierte und unsulfonierte
    O-Phenylen-CO-Einheiten sowie sulfonierte und unsulfonierte
    O-Phenylen-O-Einheiten in beliebiger Reihenfolge zueinander stehen können,

    und wobei Ar, Ar', M, x, n, m, y und p folgende Bedeutung haben:
    Ar   steht für einen Phenylenring mit p- und/oder m-Bindungen,
    Ar'   steht für eine Phenylen-, Naphthylen-, Biphenylen-, Anthrylen- oder eine
          andere zweiwertige aromatische Einheit,
    x, n und m sind unabhängig voneinander 0 oder 1,
    y   ist 0,1,2 oder 3,
    p   ist 1,2,3 oder 4
    M steht, unter Berücksichtigung der ionischen Wertigkeiten, für eines oder
    mehrere Elemente ausgewählt aus der folgenden Gruppe: H, NR_4, mit R= H, C_1-
    C_4-Alkyl-, oder ein Metall, bevorzugt ein Alkali- oder Erdalkalimetall oder ein
    Metall der 8. Nebengruppe.

2. Sulfoniertes aromatisches Polyetherketon nach Anspruch 1, dadurch
    gekennzeichnet, daß es Einheiten der Formel (III) enthält.

23

3. Sulfoniertes aromatisches Polyetherketon nach Anspruch 1, dadurch gekennzeichnet, daß es Einheiten der Formel (IV) enthält.

4. Sulfoniertes aromatisches Polyetherketon nach Anspruch 1, dadurch gekennzeichnet, daß es Einheiten der Formel (V) enthält.

5. Sulfoniertes aromatisches Polyetherketon nach Anspruch 1, dadurch gekennzeichnet, daß es mindestens zwei Einheiten der Formel (II), (III), (IV), (V) oder (VI) enthält.

6. Verfahren zur Herstellung eines sulfonierten Polyetherketons bei dem 1 % bis 100 % der O-Phenylen-CO-Einheiten mit einer SO_3M-Gruppe substituiert sind, durch Lösen eines Polyetherketons der allgemeinen Formel (I)

$$[Ar-O-]_q-Ar-[[CO-Ar'-]_r-O-Ar]_s-[CO-Ar'-]_t-[O-Ar-]_u-CO-] \qquad (I)$$

wobei Ar, Ar', q, r, s, t und u die folgende Bedeutung besitzen:

Ar   ist ein Phenylenring mit p- und/oder m-Bindungen,

Ar'   ist eine Phenylen-, Naphthylen-, Biphenylen-, Anthrylen- oder eine andere zweiwertige aromatische Einheit,

r, u und s sind unabhängig voneinander 0 oder 1,

t   ist 0,1,2 oder 3 und

q   ist 1,2,3 oder 4

in Schwefelsäure von 94 bis 97 Gew.-%, Versetzen der erhaltenen Lösung bei einer geeigneten Temperatur mit einem sulfonierenden Agens und Aufarbeitung des so erhaltenen Reaktionsansatzes sobald der gewünschte Sulfonierungsgrad der O-Phenylen-CO-Einheiten erreicht ist und gegebenenfalls Überführung der Sulfonsäuregruppen in ihre Salzform.

7.   Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die Lösetemperatur im Bereich von 10 bis 80 °C liegt.

8.   Verfahren nach mindestens einemder Ansprüche 6 bis 7, dadurch gekennzeichnet, daß die Sulfonierungstemperatur im Bereich von 10 bis 100°C liegt.

9.   Verfahren nach mindestens einem der Ansprüche 6 bis 8, dadurch gekennzeichnet, daß nach Zugabe des sulfonierenden Agens die Temperatur der Lösung mindestens 30°C beträgt.

10. Verfahren nach mindestens einem der Ansprüche 6 bis 9, dadurch gekennzeichnet, daß als Sulfonierungsagens Schwefelsäure, rauchende Schwefelsäure, Oleum, Chlorsulfonsäure, Schwefeltrioxid oder Mischungen dieser Verbindungen verwendet werden.

11. Verfahren nach mindestens einem der Ansprüche 6 bis 10, dadurch gekennzeichnet, daß man das in Schwefelsäure gelöste Polyetherketon mit Oleum versetzt, bis die Schwefelsäure-Konzentration 98 bis 100 Gew.-% oder die Oleumkonzentration 0,01 bis 15 Gew.-% SO_3 beträgt.

12. Verfahren nach mindestens einem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß der Rest Ar' für Phenylen steht.

13. Verfahren nach mindestens einem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß man ein aromatisches Polyetherketon einsetzt, das ein Copolymer darstellt, das aus mindestens zwei unterschiedlichen Einheiten der Formeln (II), (III), (IV), (V) und (VI) aufgebaut ist.

14. Verfahren nach mindestens einem der Ansprüche 6 bis 11, dadurch gekennzeichnet, daß man Mischungen verschiedener aromatischer Polyetherketone einsetzt, bei denen mindestens eines aus Einheiten der Formeln (III), (IV), (V) oder (VI) aufgebaut ist.

15. Verfahren nach mindestens einem der Ansprüche 6 bis 14, dadurch gekennzeichnet, daß man ein aromatisches Polyetherketon einsetzt, dessen nicht sulfonierbare Einheiten CO-Phenylen-CO-Einheiten sind.

16. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Polyetherketon die allgemeine Formel (III) hat, in Schwefelsäure von 95 bis 97 Gew.-% bei maximal 80°C gelöst wird und in Schwefelsäure von 95 bis 99 Gew.-% bei Temperaturen von 10 bis 80°C sulfoniert wird.

17. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Polyetherketon die allgemeine Formel (IV) hat, in Schwefelsäure von 95 bis 97 Gew.-% bei maximal 80°C gelöst wird und in Schwefelsäure von 95 bis 97 Gew.-% bei Temperaturen von 30 bis 90°C sulfoniert wird.

18. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Polyetherketon die allgemeine Formel (V) hat, in Schwefelsäure von 95 bis 97 Gew.-% bei maximal 80°C gelöst wird und bei Temperaturen von 50 bis 100°C sulfoniert wird.

19. Verfahren zur Herstellung eines sulfonierten Polyetherketons durch Lösen des Polyetherketons in Schwefelsäure von 94 bis 97% Gew.-%, Sulfonieren des Polyetherketons in Schwefelsäure, rauchender Schwefelsäure, Oleum, Chlorsulfonsäure oder Mischungen hieraus und Aufarbeitung des Reaktionsansatzes sobald der gewünschte Sulfonierungsgrad erreicht ist,

26

dadurch gekennzeichnet, daß 1 bis 100 % der O-Phenylen-CO-Einheiten mit einer SO₃M-Gruppe substituiert sind.

20. Polymerelektrolytlösung enthaltend ein sulfoniertes aromatisches Polyetherketon nach mindestens einem der Ansprüche 1 bis 5.

21. Polymerelektrolytlösung nach Anspruch 20, dadurch gekennzeichnet, daß sie zu mindestens 1 Gew.-% Polyetherketone der Formeln (II), (III), (IV), (V) und/oder (VI) enthält.

22. Polymerelektrolytlösung nach Anspruch 20, dadurch gekennzeichnet, daß sie als Hauptbestandteil eins oder mehrere aprotische dipolare Lösemittel enthält.

23. Polymerelektrolytlösung nach Anspruch 20, dadurch gekennzeichnet, daß sie ein weiteres, gegebenenfalls unsulfoniertes Polymer und gegebenenfalls geringe Anteile von Hilfsstoffen enthält.

24. Verwendung der Polymerelektrolytlösung nach mindestens einem der Ansprüche 20 bis 23 zur Herstellung von asymmetrischen Membranen.

25. Verwendung der Polymerelektrolytlösung nach mindestens einem der Ansprüche 20 bis 23 zur Herstellung von dichten Filmen.

26. Verwendung der Polymerelektrolytlösung nach mindestens einem der Ansprüche 20 bis 23 zur Erreichung eines besonders intensiven Kontaktes zwischen zwei Polymerelektrolytoberflächen.

27. Verwendung der Polymerelektrolytlösung nach mindestens einem der Ansprüche 20 bis 23 zur Erreichung einer porösen oder rauhen Oberfläche nach Kontaktieren der Lösung mit einem Fällungsmittel.

27

28. Verwendung eines Polymers nach mindestens einem der Ansprüche 1 bis 5 zur Herstellung einer Polymerelektrolytlösung und/oder zur Herstellung eines Polymerfilms.

29. Verwendung eines Polymers nach mindestens einem der Ansprüche 1 bis 5 und/oder 28 in elektrochemischen Zellen, z.B. Brennstoffzellen oder Elektrolysezellen.

30. Filme mit einer Dicke von 5 μm bis 1 mm, dadurch gekennzeichnet, daß sie einen Polymerelektrolyt nach mindestens einem der Ansprüche 1 bis 5 enthalten.

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   C08G65/48   H01M10/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   C08G   H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 575 807 (HOECHST) 29 December 1993 see page 6, line 38 - line 50; claims 4-14 see page 4, line 35 - line 45 see page 6, line 25 - line 38	1-30
Y	see page 4, line 1-8	6-19

X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 89-013709 XP002003196 & JP,A,63 291 920 (SUMITOMO) see abstract	1-5, 20-30

Y	EP,A,0 041 780 (ICI) 16 December 1981 see page 1, line 18 - line 21	6-19

Y	EP,A,0 008 895 (ICI) 19 March 1980 see page 1, line 25 - line 30	6-19

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Date of the actual completion of the international search	Date of mailing of the international search report
15 May 1996	11. 07. 96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Devriese, K

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-575807	29-12-93	CA-A-	2098159	12-12-93
		JP-A-	6049202	22-02-94
		US-A-	5362836	08-11-94
EP-A-41780	16-12-81	JP-C-	1593051	14-12-90
		JP-B-	2016335	16-04-90
		JP-A-	57025328	10-02-82
		US-A-	4419486	06-12-83
EP-A-8895	19-03-80	EP-A,B	0008894	19-03-80
		EP-A,B	0029633	03-06-81
		JP-C-	1512209	09-08-89
		JP-A-	55036296	13-03-80
		JP-B-	63051174	13-10-88
		JP-C-	1390886	23-07-87
		JP-A-	55048222	05-04-80
		JP-B-	61036781	20-08-86
		JP-C-	1650209	30-03-92
		JP-B-	3012094	19-02-91
		JP-A-	62089730	24-04-87
		JP-C-	1584173	22-10-90
		JP-A-	59074128	26-04-84
		JP-B-	62028169	18-06-87
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		US-A-	4273903	16-06-81
		US-A-	4268650	19-05-81

INTERNATIONALER RECHERCHENBERICHT

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES

IPK 6 C08G65/48 H01M10/40

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)

IPK 6 C08G H01M

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
X	EP,A,0 575 807 (HOECHST) 29.Dezember 1993 siehe Seite 6, Zeile 38 - Zeile 50; Ansprüche 4-14 siehe Seite 4, Zeile 35 - Zeile 45 siehe Seite 6, Zeile 25 - Zeile 38	1-30
Y	siehe Seite 4, Zeile 1-8 ---	6-19
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 89-013709 XP002003196 & JP,A,63 291 920 (SUMITOMO) siehe Zusammenfassung ---	1-5, 20-30
Y	EP,A,0 041 780 (ICI) 16.Dezember 1981 siehe Seite 1, Zeile 18 - Zeile 21 ---	6-19

-/--

| X | Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen | X | Siehe Anhang Patentfamilie |

* Besondere Kategorien von angegebenen Veröffentlichungen :

'A' Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist

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'&' Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
15.Mai 1996	11. 07. 96

Name und Postanschrift der Internationale Recherchenbehörde	Bevollmächtigter Bediensteter
Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Devriese, K

Formblatt PCT/ISA/210 (Blatt 2) (Juli 1992)

Int   onales Aktenzeichen

PCT/EP 96/01177

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
Y	EP,A,0 008 895 (ICI) 19.März 1980 siehe Seite 1, Zeile 25 - Zeile 30 -----	6-19

Im Recherchenbericht angeführtes Patentdokument	Datum der Veröffentlichung	Mitglied(er) der Patentfamilie		Datum der Veröffentlichung
EP-A-575807	29-12-93	CA-A-	2098159	12-12-93
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		US-A-	5362836	08-11-94
EP-A-41780	16-12-81	JP-C-	1593051	14-12-90
		JP-B-	2016335	16-04-90
		JP-A-	57025328	10-02-82
		US-A-	4419486	06-12-83
EP-A-8895	19-03-80	EP-A,B	0008894	19-03-80
		EP-A,B	0029633	03-06-81
		JP-C-	1512209	09-08-89
		JP-A-	55036296	13-03-80
		JP-B-	63051174	13-10-88
		JP-C-	1390886	23-07-87
		JP-A-	55048222	05-04-80
		JP-B-	61036781	20-08-86
		JP-C-	1650209	30-03-92
		JP-B-	3012094	19-02-91
		JP-A-	62089730	24-04-87
		JP-C-	1584173	22-10-90
		JP-A-	59074128	26-04-84
		JP-B-	62028169	18-06-87
		JP-C-	1594860	27-12-90
		JP-B-	2017571	20-04-90
		JP-A-	61043630	03-03-86
		SE-A-	7808919	25-02-79
		US-A-	4273903	16-06-81
		US-A-	4268650	19-05-81

(12) # EUROPEAN PATENT APPLICATION

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(54) Sulphonated polyarylethersulphone copolymers and process for the manufacture thereof.

(57) A polyarylethersulphone copolymer which is a hydrophilic sulphonated copolymer derived by controllably sulphonating a copolymer having the repeat unit of formula

A

together with the repeat unit B of formula

B

substantially all the units A being sulphonated after sulphonation and substantially all the units B remaining non-sulphonated after sulphonation. The sulphonation is effected using 98% w/w sulphuric acid.

EP 0 008 894 A1

SULPHONATED POLYARYLETHERSULPHONE COPOLYMERS

The present invention relates to certain sulphonated polyarylethersulphone copolymers.

We have found that polyarylethersulphone polymers
5 containing only the repeat units of formula

dissolve in concentrated sulphuric acid (98% w/w) and sulphonate very rapidly to give completely water-soluble products, probably due to the substitution of $-SO_2OH$
10 groups in all or most of the aromatic rings in the sub-units

of the polymer (see Examples 7 to 9), monosulphonation occurring in the case of the polymers with ortho or para
15 disposed ether linkages in the sub-units and disulphonation occurring in the polymers with meta disposed linkages in the sub-units.

By contrast we have found that the polyarylether-sulphones containing only the repeat unit of formula

20   B

are virtually non-susceptible to sulphonation in concentrated sulphuric acid (98% w/w), the sulphuric acid dissolving the polymer but not changing it, (see Example 10), even though other sulphonating agents such
25 as oleum and chlorosulphonic acid, and even a mixture of concentrated sulphuric acid with a little oleum, completely sulphonate the polymer and/or degrade it (see Examples 11 and 12). Consequently polyarylethersulphone

copolymers containing repeat units A and B may be
controllably sulphonated in concentrated sulphuric acid
(98% w/w) to give hydrophilic sulphonated copolymers
(ranging up to completely water soluble polymers) by
5   varying the proportion of the repeat unit B in the
copolymer.

According to the present invention there is provided
a polyarylethersulphone copolymer which is a hydrophilic
sulphonated copolymer derived by controllably sulphonating
10   a copolymer having the repeat unit of formula

A $-O-\langle\!\langle\,\rangle\!\rangle-O-\langle\!\langle\,\rangle\!\rangle-SO_2-\langle\!\langle\,\rangle\!\rangle-$

together with repeat unit of formula

$-O-\langle\!\langle\,\rangle\!\rangle-SO_2-\langle\!\langle\,\rangle\!\rangle-O-\langle\!\langle\,\rangle\!\rangle-SO_2-\langle\!\langle\,\rangle\!\rangle-$

substantially all the units A being sulphonated after
15   sulphonation and substantially all the units B remaining
non-sulphonated after sulphonation.

The polyarylethersulphone copolymer of the invention
is preferably one derived by sulphonating a copolymer
which has 1 to 99 mole % of units A and 99 to 1 mole % of
20   units B, and in particular a copolymer which has 5 to 80
mole % of units A and 95 to 20 mole % of units B.

The control of the sulphonation reaction should be
such that the resulting copolymer preferably has a degree
of hydrophilicity corresponding to a water absorption
25   capacity at ambient temperature of about 2 weight % water
absorption to complete solubility in water.

The hydrophilic polymers of the invention (which
preferably absorb 2-40 weight % water, particularly 5-30
weight % water, at ambient temperature) are potentially
30   useful as membrane materials, e.g. for ultra-filtration

processes, e.g. desalination and removal of micro-organisms, since they are not only hydrophilic in character but retain considerable strength even when containing a significant quantity of water (e.g. up to 20 weight % water) (see Example 5).

Ionomers of the above-defined copolymers which are sulphonated with $-SO_2OH$ groups may be readily prepared e.g. by converting the $-SO_2OH$ groups to salts such as SO_3-M^+ (where M = an alkali metal or NR_4, R being an alkyl group); these too have utility as hydrophilic polymers. Accordingly, the sulphonyl groups of the copolymers of the invention preferably have the formula $-SO_2Y$ where Y is H, an alkali metal, or NR_4 where R is an alkyl group.

Copolymers having the repeat units A and B may be conveniently prepared by condensation of the appropriate dihydroxy phenol (e.g. hydroquinone, catechol or resorcinol), 4,4'-dihydroxydiphenylsulphone and 4,4'-dichlorodiphenylsulphone, and an alkali metal carbonate or bicarbonate in the presence of a sulphone or sulphoxide solvent, using the method of preparing polyarylene polyethers described in Canadian Patent 847 963.

The present invention is now illustrated by the following examples.

EXAMPLE 1

A copolymer (20 gms) of repeat units A (para disposed ether linkages in sub-units) and B containing 25 mole % of units A (and correspondingly 75 mole % of units B) was shaken for 18 hours with concentrated sulphuric acid (98% w/w) (110 ml) to give a very viscous solution. Further (50 ml) concentrated sulphuric acid was added and shaking continued for a further 18 hours (i.e. 36 hours in all).

This solution was then poured into distilled water (800 ml) in a Waring blender, to give a white precipitate which was filtered and washed 3 times with fresh water in

the blender, being separated by filtration after each
wash.

The product was dried overnight at about 65°C in a
vacuum oven.

5   Copolymers of repeat units A (para disposed ether
linkages in sub-units) and C of different composition
(varying from 25 mole % A to 66.7 mole % A and
correspondingly 75 mole % B to 33.3 mole % B) were used in
this Example. All the prepared products after analysis by
10   220 MHz nmr spectroscopy indicated monosulphonation on
substantially all of the sub-repeat units

$$-O-\langle\!\!\langle\ \rangle\!\!\rangle-O-$$

in the polymer chain but no sulphonation on any of the
repeat units B. All the products were soluble in dimethyl
15   formamide and dimethylsulphoxide.

EXAMPLE 2

A copolymer (5 g) of repeat units A (para disposed
ether linkages in sub-units) and B containing 80 mole % A
and 20 mole % B was shaken overnight with concentrated
20   sulphuric acid (98% w/w) (20 ml). Further (20 ml)
concentrated sulphuric acid was added and shaking
continued for a further 24 hours. This solution was then
poured into distilled water in a Waring blender to give a
white precipitate which was filtered and washed 4 times
25   with water, and dried overnight in a vacuum oven.

Copolymers of repeat units A (para disposed ether
linkages in sub-units) and B containing respectively 5
mole % A/95 mole % B, 90 mole % A/10 mole % B, 40 mole %
A/60 mole % B were sulphonated in a similar fashion to the
30   copolymer 80 mole % A/20 mole % B, although starting from
different quantities of copolymer and using different
amounts of concentrated sulphuric acid.

The products were analysed by 220 MHz spectroscopy and indicated monosulphonation on substantially all of the sub-repeat units

5 in the polymer chain but no sulphonation on any of the repeat units B.

EXAMPLE 3

The sodium salts of the sulphonated copolymers of Example 2 were prepared by neutralisation in excess NaOH
10 solution. The neutralisation of the sulphonated 10 mole % A/90 mole % B copolymer is described as a typical example.

The sulphonated 10 mole % A/90 mole % B copolymer of Example 2 (50 g) was stirred overnight in a solution of
15 NaOH (30 g) in water (600 ml). The mixture was then heated at 60-80°C all day and cooled to 40°C. The product was filtered, washed 4 times with water and oven dried.

The sodium contents of the sulphonated 10 mole % A/ 20 mole % B, 20 mole % A/80 mole % B and 40 mole % A/
20 60 mole % B copolymers were determined using flame emission spectroscopy (FES) and confirmed the nmr spectroscopic analysis indicating that substantially all the units A had been monosulphonated. The results were as follows:

25 Molar Ratio A/B in copolymer	Na content of sulphonated copolymer found by FES	Monosulphonation of units A requires
10/90	0.53%	0.58%
20/80	1.20%	1.00%
40/60	2.30%	2.06%

EXAMPLE 4

The water absorption of the copolymers of Example 2
before sulphonation and after sulphonation, and also of
the neutralised sulphonated copolymers of Example 3, were
5 measured after steeping initially dry films of the
copolymers (cast from solution in dimethyl formamide) in
water for 24 hours at ambient temperature. The results
were as follows:

Molar Ratio A/B in copolymer	Water absorption (weight %) of copolymer before sulphonation (Example 2)	Water absorption (weight %) of sulphonated copolymer (Example 2)	Water absorption of (weight %) of neutralised sulphonated copolymer (Example 3)
5/95	2.4	4.5	2.4
10/90	2.5	4.4	3.6
20/80	2.3	4.5	5.5
40/60	3.9	8.9	13.1
80/20	not measured	not measured	36.6

10   ## EXAMPLE 5

The sulphonated 40 mole % A/60 mole % B and
80 mole % A/20 mole % B copolymers of Example 2 were
tested in the form of cast film for mechanical properties,
both dry and after absorption of moisture. For comparison
15 purposes a homopolymer containing units B only (not
sulphonated) was also tested. The results were as
follows:

Polymer Used		Water Content (wt %)	1% Secant Modulus (NMm^{-2})	Yield Stress (NMm^{-2})	Tensile Strength (NMm^{-2})	Elongation at break (%)
Homo-polymer of	Dry	–	1450	–	74	8.2
units B	Wet	1.0	1350	–	–	–
Sulphon-ated copolymer 40 mole % A/	Dry	–	1700	68	62	10.1
60 mole % B	Wet	8.3	1500	45	–	–
Sulphon-ated copolymer 80 mole % A/	Dry	–	1750	59	47	14.7
20 mole % B	Wet	19.5	1030	32	26	32.1

(– indicates not measured)

EXAMPLE 6

A copolymer (5 g) of repeat units A (meta disposed ether linkages in sub-units) and B containing 40 mole % A and 60 mole % B was dissolved in concentrated sulphuric acid (98% w/w) and left for 36 hours. This solution was poured into distilled water to give a precipitate which was filtered, washed 3 times with water and oven dried. The product was analysed by 220 MHz spectroscopy and indicated disulphonation on substantially all of the sub-repeat units

in the polymer chain but no sulphonation on any of the repeat units B.

The water absorption of the copolymer was measured
after steeping an initially dry film of the copolymer
(cast from solution in dimethyl formamide) in water for 24
hours at ambient temperature; the value obtained was 7.5
5   weight %.

EXAMPLE 7

A homopolymer of repeat unit A (para disposed ether
linkages in sub-units) (10 g) was dissolved in
concentrated sulphuric acid (98% w/w) with stirring and
10   samples (50 ml) removed from time to time and precipitated
in dilute sulphuric acid or saturated sodium sulphate; the
polymer samples corresponding to the various times of
sulphonation were analysed by 220 MHz nmr spectroscopy as
solutions in dimethyl sulphoxide and found to have the
15   following properties:

1 hour	.85% of the units bore an $-SO_2OH$ group (isolated as Na salt).
2 hours	99% of the units bore an $-SO_2OH$ group (isolated as Na salt).
4.5 hours	100% of the units bore an $-SO_2OH$ group (isolated as Na salt).
23 hours	98% of the units bore an $-SO_2OH$ group (isolated as free acid).

Substantially all the sub-units bore one $-SO_2OH$ group.

25   ### EXAMPLE 8

A homopolymer of repeat unit A (ortho disposed ether
linkages in sub-units) was sulphonated in concentrated
sulphuric acid (98% w/w) and the product analysed by 220
MHz nmr spectroscopy as a solution in the concentrated
30   sulphuric acid (the product would not precipitate by
pouring the acid solution into water). As with the homo-
polymer of repeat unit A (para disposed ether linkages in
sub-units) the product was found to have sulphonated
rapidly with substantially all the sub-units bearing one
35   $-SO_2OH$ group.

EXAMPLE 9

A homopolymer of repeat unit A (meta disposed ether linkages in sub-units) was sulphonated in concentrated sulphuric acid (98% w/w) and the product analysed by 220
5 MHz nmr spectroscopy as a solution in the concentrated sulphuric acid (the product would not precipitate by pouring the acid solution into water). As with the homopolymers of repeat unit A (para or ortho disposed ether linkages in the sub-units) the product was found to
10 have sulphonated rapidly; substantially all the sub-units bore two $-SO_2OH$ groups however.

EXAMPLE 10

A homopolymer containing the repeat unit B (50 g) was dissolved in concentrated sulphuric acid (98% w/w)
15 (200 ml), left for 72 hours, precipitated in dilute sulphuric acid, washed, macerated and dried. The infra-red and nmr spectra of the product showed it to be indentical with the starting material.

EXAMPLE 11

20 A homopolymer containing the repeat unit B (20 g) was added to chlorosulphonic acid (100 ml). Slight effeverence was apparent and white fumes were evolved. After standing overnight (the total time of the polymer in the acid being 20 hours), the solution was poured into
25 300 ml of concentrated sulphuric acid (98% w/w) and this solution then poured onto ice. A very fine precipitate resulted, which filtered very slowly and was washed once with water and then dried. The product appeared to be almost entirely soluble in water - indicating a high
30 degree of sulphonation.

EXAMPLE 12

A homopolymer of repeat unit B (20 g) was mixed with oleum (150 ml) and left overnight. The resulting black solution still contained undissolved polymer and so the
35 mixture was stirred for a further 5 hours, and then poured

into water. No precipitate was obtained, but instead a
brownish/orange solution was obtained. The product was
discarded, being assumed to be highly sulphonated or
entirely degraded.

5   In another experiment, the homopolymer of repeat
unit B (15 g) was dissolved in concentrated sulphuric
acid (98% w/w); oleum (50 ml) was then added and the
solution stirred for 30 minutes and then poured onto ice
and left overnight. A rubbery white solid was
10   precipitated and was washed and dried. This product was
found to be highly sulphonated.

CLAIMS

1. A polyarylethersulphone copolymer which is a hydrophilic sulphonated copolymer derived by controllably sulphonating a copolymer having the repeat unit of formula

5   A $-O-\langle\!\!\!\langle\rangle\!\!\!\rangle-O-\langle\!\!\!\langle\rangle\!\!\!\rangle-SO_2-\langle\!\!\!\langle\rangle\!\!\!\rangle-$

together with the repeat unit of formula

B $-O-\langle\!\!\!\langle\rangle\!\!\!\rangle-SO_2-\langle\!\!\!\langle\rangle\!\!\!\rangle-O-\langle\!\!\!\langle\rangle\!\!\!\rangle-SO_2-\langle\!\!\!\langle\rangle\!\!\!\rangle-$

substantially all the units A being sulphonated after sulphonation and substantially all the units B remaining
10 non-sulphonated after sulphonation.

2. A polyarylethersulphone copolymer according to claim 1 derived by controllably sulphonating a copolymer which has 1 to 99 mole % of units A and 99 to 1 mole % of units B.

15   3. A polyarylethersulphone copolymer according to claim 2 derived by controllably sulphonating a copolymer which has 5 to 80 mole % of units A and 95 to 20 mole % of units B.

4. A polyarylethersulphone copolymer according to
20 claim 1 having a hydrophilicity corresponding to a water absorbtion capacity at ambient temperature of 2 weight % water absorption to complete solubility in water.

5. A polyarylethersulphone copolymer according to claim 4 having a hydrophilicity corresponding to a water
25 absorption capacity at ambient temperature of 2 to 40 weight %.

6. A polyarylethersulphone copolymer according to any one of the preceding claims in which the sulphonyl groups on the copolymer have the formula $-SO_2OY$ where Y
30 is H, Cl, an alkali metal or NR_4 where R is an alkyl group.

7.   A polyarylethersulphone copolymer according to any one of the preceding claims in the form of a membrane.

8.   A process for the production of a hydrophilic polyarylethersulphone copolymer which comprises controllably sulphonating using concentrated sulphuric acid (98% w/w) a copolymer having the repeat unit of formula

A

together with the repeat unit of formula

B

to produce a sulphonated copolymer in which substantially all the units A are sulphonated and substantially all the units B are non-sulphonated.

9.   A process according to claim 8 wherein the copolymer which is sulphonated has 1 to 99 mole % of units A and 99 to 1 mole % of units B.

10.   A process according to claim 9 wherein the copolymer which is sulphonated has 5 to 80 mole % of units A and 95 to 20 mole % of units B.

11.   A process according to any one of claims 8 to 10 wherein after sulphonation with the concentrated sulphuric acid (98% w/w), the $-SO_2OH$ groups formed on the polymer are converted to groups of formula $-SO_2OM$ where M is an alkali metal or NR_4 where R is an alkyl group.

European Patent
Office

EUROPEAN SEARCH REPORT

0008894

Application number

EP 79 301 674.2

DOCUMENTS CONSIDERED TO·BE RELEVANT				CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages		Relevant to claim	
A	US - A - 4 054 707 (J.P. QUENTIN) * claims 1, 4, column 1, line 64 to column 2, line 5 * --		1, 8, 11	C 08 G 75/23 C 08 G 85/00
A	US - A - 3 709 841 (J.P. QUENTIN) * claims 1, 3; column 2, lines 3 to 17 and line 27 * --		1, 8	
A	HOUBEN-WEYLS "Methoden der organischen Chemie" 4th edition, vol. IX 1955, G. THIEME VERLAG, Stuttgart, * pages 460 and 471 * --			TECHNICAL FIELDS SEARCHED (Int.Cl.³) C 08 F 8/00 C 08 G 65/00 C 08 G 75/00 C 08 G 85/00 C 08 J 7/00 C 08 L 81/00
A	W. FOERST "Ullmanns Encyklopädie der technischen Chemie" 3rd edition, vol. 14, 1963, URBAN AND SCHWARZENBERG, München, Berlin * pages 595 to 597 * ----			

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	03-12-1979	MARX

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Contents

11

Heterochain Block Copolymers*

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University of Bradford, UK

11.1 INTRODUCTION AND HISTORICAL SURVEY

This chapter is concerned with block copolymers having, in at least one type of the constituent blocks, atoms of an element or elements other than carbon as recurrent structural features of the main chain. Substances conforming to this general description were the earliest block copolymers to be studied, and the class includes some of the present day technologically most important block macromolecular materials.

The history of synthetic heterochain block copolymers began effectively in the early 1940s with the introduction of Bayer's 'diisocyanate polyaddition procedure' as a method for the linking together of molecules of preformed aliphatic polyesters, poly(ester amide)s and similar substances to obtain elastomers.[1-6] At that time ideas of elastomer structure and properties were dominated by experience with natural rubber, and there was a prevalent belief that covalent crosslinking was an indispensable prerequisite for serviceability in such materials. The thinking of Bayer and his co-workers was therefore directed largely towards cast elastomers containing network structures, though it is now apparent that at least some of their interesting products were of linear block polymeric character. The work of that period led eventually to the now well-known linear poly(ester urethane) and poly(ether urethane) thermoplastic block copolymer elastomers and to the elastic ('spandex') fibres in both of which groups the recovery properties and restraint to viscous flow arise from physical constitutional factors rather than from a system of covalent crosslinks.

A second fertile theme in heterochain block copolymers developed from work in the late 1940s by Coleman[7] whose interest in modifying the properties of poly(ethylene terephthalate) fibres was influenced by knowledge (new at that time) of the molecular structure of silk fibroin which had been recognized to be partially of block character. On the basis of this model, poly(oxyethylene) blocks

were introduced into the polyester chain structure yielding fibre-forming materials of improved hydrophilicity and dyestuff receptivity. The melting temperatures of the copolymers, unlike those of random copolymers with similar weight percentages of modifying units, were not greatly reduced from that of the homopolyester, leading to the conclusion (which has significance for block copolymers generally) that this property is determined by the molar rather than the weight fraction of modifying unit. Coleman's investigation was restricted to essentially hard copolymers containing limited amounts of combined polyether units. The composition range was later widened by Charch and Shivers[6] who found that the incorporation of larger amounts (40–70 wt %) of polyether unit gave elastomeric products with good tensile recovery and stress decay characteristics. From this pattern of a linear chain structure composed of high melting readily crystallizable hard segments intercalated with low melting soft segments there has developed the important group of thermoplastic poly(ether ester) and block copolyester elastomers which appeared as commercial materials in the 1970s.

The third class of novel heterochain block copolymers, inspired by interest in non-ionic detergents, was evolved in the early 1950s by Lundsted and co-workers[9-11] who found that substances composed of a central poly(oxypropylene) unit, itself having a sufficient MW (> 900) to be insoluble in water as a homopolymer and flanked by poly(oxyethylene) blocks, were water-soluble liquids or solids, according to the lengths of the end blocks, with valuable surfactant and detergent properties.

Subsequent developments, which have greatly expanded the range of heterochain block copolymers, form the main subject of this chapter and will be mentioned here only in outline. The discovery by Szwarc of methods for achieving sequential polymerizations by homogeneous termination-free ('living') reactions of vinyl monomers has led not only to the well-established polyvinyl–polydiene block polymer elastomers but also to procedures of wide potential for combining polyvinyl species with heterochain block species through a variety of strategies of synthesis.[12-15] The late 1950s also saw the start of work on polysiloxane-containing block copolymers[16-19] of which those with poly(oxyalkylene) co-units quickly gained industrial importance as stabilizing surfactants for the control of cell growth and form in the manufacture of flexible polyurethane foams.[20]

Until well into the 1960s interest in block copolymers as bulk materials was centred particularly upon those of elastomeric character but investigation has since developed on plastics materials of block or segmented character, especially those containing aromatic polycarbonate or polysulfone sequences.[21-25] The 1970s brought an extension and intensification of work in these directions together with the introduction of new themes of study—both for carbochain and heterochain block polymers—in, for example, polyionic materials,[26-34] copolymers containing blocks of naturally occurring macromolecules,[35-40] and the use of block copolymers as catalysts.[41-43]

These utilitarian developments have naturally been accompanied by a large body of fundamental investigation, partly concerned with the evolution of new methods of synthesis and partly with the exploration of that inner texture of block copolymers which confers their distinctive properties and differentiates them from random copolymers. The phase-separated character of amorphous polyvinyl–polydiene block polymers has been recognized and investigated intensively since the later 1960s.[311] For heterochain block copolymers, which are of more polar character and often semi-crystalline, the elucidation of supramolecular organization is a more complex undertaking which calls, for its resolution, on the whole armamentarium of modern polymer physics. Advances in this field have been a notable feature of the later 1970s.

Detailed accounts of earlier work on heterochain block copolymers are given in two standard monographs published during the 1970s.[44,45] The present chapter will necessarily cover some of the ground in order to establish the context for consideration of later developments which are surveyed up to the end of 1980. The approach throughout will be illustrative rather than encyclopedic, with regard to synthesis of some selected block copolymers.

11.1.1 Nomenclature and Symbolism

The development of any science depends upon the ability of its practitioners to communicate in precise terms and to retrieve information from original and secondary sources without loss or distortion of meaning. These requirements would ordinarily presuppose the existence of a pertinent lingua franca. Even for relatively simple homopolymers, however, nomenclature and classification presents a complex and incompletely resolved problem,[46,47] and no generally accepted system yet exists for the naming of block copolymers so as to describe precisely their chemical composition and molecular structural organization. Some examples of the difficulties are given below.

(a) No firm level of definition exists as to the molecularity appropriate for a component of a copolymer structure to be recognized as a 'block'. Conventionally the term is often applied to any

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structural component which is of sufficient size to display in the copolymer some characteristic feature(s) of the corresponding free homopolymer, yet this view would exclude the case where polymeric blocks of one component are joined together by a small linking group which may modify considerably the properties of the major component without displaying its own homopolymer character. Such copolymers are sometimes termed segmented polymers but this term is also frequently used as synonymous with block polymers; another common designation for these materials is as chain-extended or simply extended polymers.

(b) Many block copolymers are synthesized by the direct or indirect combination of preformed, relatively low MW polymeric precursors furnished with reactive end groups. Such precursors are known variously — and sometimes with different nuances of meaning — as prepolymers, telechelic polymers, oligomers, macromers, segmers or as end-capped or tipped polymers. For uniformity, such precursors will be described as oligomers throughout this chapter.

(c) A typical procedure for the synthesis of some classes of block copolymers commences with the living polymerization of a monomer, *e.g.* styrene, initiated bidirectionally by a dianion, *e.g.* the tetrameric dianion derived from α-methylstyrene (A). When all of the styrene has been polymerized, the reactivity of the anionic chain ends is modified by treatment with a reagent B so as to permit sequential polymerization with a second monomer C; the ensuing living block copolymer is finally stabilized by treatment with a reagent D. The product, which has the general structure D′(poly-C′)—B′—(polystyrene)—(A′)₄—(polystyrene)—B′—(poly-C′)—D′ (1) where A′, B′, C′, D′ represent the residues of the original active ingredients, will often be described as poly-C-*block*-polystyrene-*block*-poly-C even though this expression pays no regard to the foreign structure fragments resulting from the various steps of chemical reaction, or to the inversion of chain direction that occurs at the centre of the (A′)₄ unit.

(d) The poly(ether ester)s already mentioned typify the class of random block copolymers which present a different problem in designation. An important group of these materials is usually prepared by the co-condensation of dimethyl terephthalate with a mixture of tetramethylene glycol (1,4-butanediol) and the oligomeric diol, $HO[(CH_2)_4O]_xH$ (2), which is itself a polyether. The relative proportions of the two diols can be varied at will, and the molecules of the products (which, strictly, are (polyether)ester–polyester block copolymers) are composed of blocks of units (3) and (4) placed randomly along the chain and with the values of y and z related to the diol proportions used.

$$[-O(CH_2)_4OCO\langle\bigcirc\rangle CO-]_y, \qquad [-O[(CH_2)_4O]_xCO\langle\bigcirc\rangle CO-]_z$$

(3)   (4)

The structure of (3) will be easily recognized from its common verbal designation as poly(tetramethylene terephthalate), though perhaps less readily from the systematic name poly(oxy-1,4-butanediyloxycarbonyl-1,4-phenylenecarbonyl) recommended by IUPAC. What, however, of (4)? The precursor oligomer (2) is named variously in the literature as polytetrahydrofuran, polytetramethylene oxide, polytetramethylene glycol, polyoxytetramethylene glycol, poly(oxytetramethylene) glycol, polytetramethylene ether glycol and polybutylene oxide glycol; the writer is aware of a case where four of these names appear in a single published paper! It will be obvious that certain of these terms are structurally inexplicit and stoichiometrically inaccurate as literal equivalents of formula (2). Additionally, they are not readily adaptable to the precise naming of (4), a particular problem arising from the 'extra' oxygen atom (with respect to the repeating unit) remaining from the left-hand hydroxyl group of (2).

An important function of nomenclature is for the storage and retrieval of information. It is therefore of interest to examine, with the help of this example, the practice of *Chemical Abstracts* — the prime chemical search tool of the Western world — which, except for a small number of macromolecular materials of well-defined structure, indexes polymers on the basis of their *supposed* monomers or precursors rather than as substances in their own right. Until 1971,[48] the substances in question were indexed under 'terephthalic acid, polyester with 1,4-butanediol and polytetramethylene glycol'. Subsequently,[49] partial use has been made of IUPAC-recommended structure-based nomenclature, leading to a cycle of expressions of the type '1,4-benzenedicarboxylic acid, polymer with 1,4-butanediol and α-hydro-ω-hydroxypoly(oxy-1,4-butanediyl)', permuted to commence with each reactant in turn. It will be noted that these terms presuppose what is not the case in practice, that terephthalic acid (1,4-benzenedicarboxylic acid) is an immediate precursor of the polymers. However, further search will show the polymers located under a cycle of names of the type 'poly(oxy-1,4-butanediyl), α-hydro-ω-hydroxy, polymer with 1,4-butanediol and dimethyl 1,4-benzenedicarboxylate', and will reveal that the assigned *Chemical Abstracts Registry* numbers, which are intended

to be unique with respect to molecular structure, are different for the phantom acid-based polymer [37282-12-5] and real ester-based polymer [9078-71-1]. Clearly the full recovery of information (and the avoidance of mis-information) on an unfamiliar block copolymer calls for a combination of skills in lexicography and chemical guesswork that it is not necessarily possessed by all polymer scientists.

Faced with these difficulties, the terminology used in this chapter will be pragmatic and semi-structural, unavoidably containing some stoichiometric imprecisions, but aiming at a reasonable middle course between the extremes of inscrutable rigour and misleading jargon. To avoid excessively cumbrous formulae and names, considerable use will be made of abbreviations, P as a generalized representation of a polymer molecule, M for a monomer and R for other reactants. Different varieties of such generalized species will be denoted by subscript letters (P_A, P_B, etc.), and reactive end groups, where the nature of these does not need to be specified precisely, by ♦ or ●. Where appropriate, block copolymers will be indicated by -*block*- between the names of the components, and random copolymers by -*co*-. Poly(alkylene terephthalates) will be abbreviated in the familiar way as 2G.T, 4G.T, etc., according to the numbers of carbon atoms in the alkylene moiety, and linear aliphatic polyesters as 2G.6, 4G.6, etc., the final cipher being the carbon number of the residue of a linear alkanedicarboxylic acid; the oxy(methyl-1,2-ethanediyl)oxy group ($-OCHMeCH_2O-$), as in poly(1,2-propylene terephthalate), will be abbreviated as 1,2-P. The simple alkyl groups from methyl to butyl will be shown in formulae as Me, Et, Pr and Bu, and generalized alkylene and arylene groups as Alk and Ar, respectively.

11.1.2 Principles of Block Copolymer Synthesis

The following brief account of the major approaches to heterochain block copolymer synthesis will serve as an introduction to the developments described in Section 11.2.

11.1.2.1 Adventitious and imperfect block copolymer syntheses

Copolymers containing some measure of ordered sequences of the component units (blockiness) result from certain ostensibly random copolymerization reaction, particularly of the condensation and step polymerization type, as a result of differential reactivities amongst the functional groups present. Thus, if a bifunctional reactant R_A (e.g. a dicarbonyl chloride) reacts with a stoichiometrically equivalent mixture of two co-reactants R_B and $R_{B'}$. which are of similar chemical type (e.g. diamines) but different reactivities such that R_A-R_B unions are formed more readily than $R_A-R_{B'}$. there may be an enrichment of the first-mentioned unions in the early stages of combination leading to partial block structure. An analogous result may occur in the reaction of R_A with bifunctional R_B which has combining groups of different reactivities; in this case the blockiness can take the form of a preference for head-to-tail combinations of the units rather than their random head-to-tail/head-to-head presentation along the chain.

Another type of adventitious block polymer formation occurs in the partial inter-randomization in the melt of mixtures of homopolymers such as polyesters and polyamides which can undergo ester–ester, amide–amide or ester–amide interchange reactions.

These procedures suffer from the deficiencies: (i) of relative structural randomness and lack of well-defined sequential specificity in the products; and (ii) of non-equilibrium character which can lead to continued group interchange and eventual complete randomization on further thermal treatment.

11.1.2.2 Synthesis by sequential polymerization

This class of reactions is represented most prominently by the living anionic polymerizations in which a first monomer M_A is converted to its corresponding polymer P_A having propagatively reactive groups at one or both ends of its chain according to whether a mono- or a bi-functional initiator is employed. The living polymer then serves as initiator for the polymerization of a second monomer M_B, yielding a diblock copolymer (5) or a triblock copolymer (6) depending on the functionality of P_A (equation 1).

The concept is open to considerable elaboration. Thus, the diblock polymer (5), whilst still reactive, may be coupled with a suitable bifunctional reagent to form a triblock copolymer (7) having P_A units at the outsides of the molecule rather than in the centre as in (6) (equation 2). The reactive forms of (5) and (6) may also be used to initiate the polymerization of a further monomer M_C to give

$$P_A \blacklozenge \xrightarrow{\;nM_A\;} P_A\text{---}P_B \qquad (5)$$

$$nM_A \xrightarrow{\text{Monofunctional initiator}} \qquad \qquad \qquad \qquad (1)$$

$$nM_A \xrightarrow{\text{Bifunctional initiator}} \blacklozenge P_A \blacklozenge \xrightarrow{\;2nM_B\;} P_B\text{---}P_A\text{---}P_B \qquad (6)$$

$$2P_A\text{---}P_B\blacklozenge \;+\; \bullet R \bullet \longrightarrow P_A\text{---}P_B\text{---}R\text{---}P_B\text{---}P_A \qquad (2)$$

$$(7)$$

products P_A---P_B---P_C (8) and P_C---P_B---P_A---P_B---P_C (9) with three species of blocks per molecule.

Success in such a continued sequential reaction depends critically upon the real natures of the substances involved, on the reactivity of the end groups existing at each stage or formed by intermediate refunctionalization, on the efficiency of the reactions employed, and upon the avoidance of interfering side reactions whether extrinsic (*e.g.* due to terminating impurities) or intrinsic (*e.g.* due to the occurrence of transfer reactions). In favourable cases the consecutive 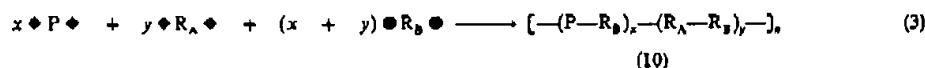stages can be achieved with high precision leading to polymers of accurately known structures composed of blocks of predetermined sizes and with narrow MW distributions ($\bar{M}_w/\bar{M}_n$ close to unity).

Of sequential polymerizations proceeding by anionic propagation, the most important from the standpoint of this chapter are those using styrene, α-methylstyrene, 1,3-butadiene or isoprene as sources of carbochain blocks, and a limited range of ring-fissile monomers selected from the classes of cyclic ethers and sulfides, lactones, lactams, siloxanes and oxazolidin-2,5-diones as sources of heterochain blocks. Recent work has opened the way to the use of living cationic systems as the basis of heterochain block copolymer synthesis with monomers such as tetrahydrofuran (oxolane) and vinyl alkyl ethers. However, despite its conceptual elegance, sequential polymerization is subject to considerable limitations with respect to the range of monomers that can be used and to the order in which they can be assembled within the polymer chain. Furthermore, the techniques required are often complex and not readily adaptable to large-scale working.

II.1.2.3 Random block polymerizations

This method of synthesis, which is indicated schematically by equation (3), comprises essentially a reaction of step copolymerization between reactants at least one of which is polymeric. Commonly met systems of this class involve combination through the end group reactant pairs HO + OCN, HO + MeO$_2$C, and NH$_2$ + ClCO.

$$x\blacklozenge P\blacklozenge \;+\; y\blacklozenge R_A\blacklozenge \;+\; (x\;+\;y)\bullet R_b\bullet \longrightarrow [\text{---}(P\text{---}R_B)_x\text{---}(R_A\text{---}R_B)_y\text{---}]_n \qquad (3)$$

$$(10)$$

In the simplest procedure (used, for example, for the synthesis of the block poly(ether ester)s already mentioned), a mixture of two reactants of similar chemical type, one being of low MW and the other oligomeric, is combined with a common co-reactant R$_B$ used in stoichiometric equivalence to the total of reactive groups in P and R$_A$. The product (10) is a multiblock copolymer composed of two types of units, one of which includes the structural residue of the starting oligomer; their relative proportions are determined by the values of x and y which can be varied at will, but their placement along the chain is statistical. The following relationships are important in relation to the bulk properties of such copolymers.

(a) Since P is oligomeric and R$_A$ of low MW, there will be a marked disparity between the weight and molar fractions of the units P---R$_B$ and R$_A$---R$_B$ in the product (10). This is illustrated by Figure 1 where curves b and d show the relationships for block copolymers in which R$_A$---R$_B$ has a MW of 200 and P---R$_B$ has MW's of 1000 and 5000, respectively. In curves a and c, the same MW's are used for P---R$_B$ but that of R$_A$---R$_B$ is taken as 350. This span of values covers that occurring in most practically important block copolymers. It is evident that quite large weight (and hence volume) fractions of the P---R$_B$ component are present even at relatively low molar fractions.

(b) In random block copolymers (10) made by conventional step polymerization reactions, both types of blocks will be polydisperse. Both x and y will thus ordinarily have a distribution of values arising from the statistics of reaction, with a range of block MW's modified further in the case of x by

374　　　　　　　　　　*Heterochain Block Copolymers*

Figure 1　Mol *vs.* wt% for P—R$_B$ blocks in [—(P—R$_B$)$_x$—(R$_A$—R$_B$)$_y$—]$_n$ multiblock copolymers

| Curve | Unit MW's | |
	P—R$_B$	R$_A$—R$_B$
a	1000	350
b	1000	200
c	5000	350
d	5000	200

Figure 2　Average segment length (repeating units) for R$_A$—R$_B$ blocks in [—(P—R$_B$)$_x$—(R$_A$—R$_B$)$_y$—]$_n$ random multiblock copolymers in relation to the weight proportion of P—R$_B$

| Curve | Unit MW's | |
	P—R$_B$	R$_A$—R$_B$
a	1000	350
b	1000	250
c	2500	250
d	5000	250

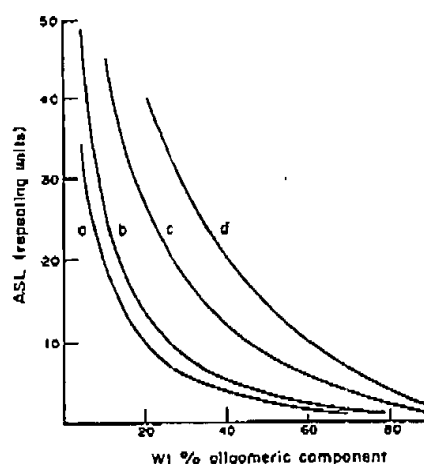the distribution existing in the starting oligomer ♦ P ♦ . The distribution in values of y is generally unknown but for purposes of comparison, as will be used later, it is helpful to discuss the molecularity of the R_A—R_B sequences in terms of a notional average segment length (ASL) calculated by assuming the copolymer molecules to be of equal size and made up by interpolating equisized P—R_B units uniformly into the poly-(R_A—R_B) chain. The average segment length is then given by

$$ASL = \frac{\text{total number of } R_A-R_B \text{ units}}{(\text{total number of P--}R_B \text{ units}) + 1}$$

Figure 2 shows the relationship for some practically important MW's of R_A—R_B and P—R_B. It can be seen that increase in the weight fraction of the oligomeric component P—R_B leads to a rapid fall in the average segment lengths of the R_A—R_B units.

Where the chemistry of synthesis permits, as in the formation of block copolyurethanes by the reaction of a diisocyanate with a short-chain diol and an oligomeric polyether- or polyester-diol which takes place at temperatures sufficiently low that group interchange is avoided, a higher order of block organization can be ach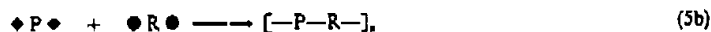ieved by using a two-stage procedure as shown in equations (4a) and (4b). In this example, three molar proportions of the oligomer P are first combined with four of the co-reactant R_B to give a prepolymer (11) which is then reacted with R_A and the necessary additional quantity of R_B to give a product (12) containing sequences of three consecutive P units.

$$3 ♦ P ♦ + 4 ● R_B ● \longrightarrow ● R_b-P-R_B-P-R_B-P-R_B ● \tag{4a}$$
$$(11)$$

$$x(11) + y ● R_B ● + (x + y) ♦ R_A ♦ \longrightarrow$$
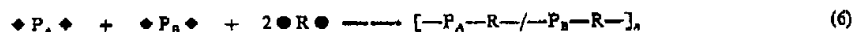$$[(-R_A-R_B-P-R_B-P-R_B-P-R_B-)_x-(-R_A-R_B-)_y-]_n \tag{4b}$$
$$(12)$$

As will be seen later, extensive variations can be made in the natures and relative proportions of the reactants, the MW of the oligomeric components, and the types of linking reactions used. Whilst the approach is less than ideal with respect to structural specificity, it is perhaps the most versatile of all methods available for the synthesis of block copolymers. Particularly important are the cases where (P—R_B)$_x$ is of low T_g (and, if crystalline, of low T_m) and (R_A—R_B)$_y$ is of high T_g, preferably crystalline and of high T_m, and hydrogen bonded. Polymers of this class are typically thermoplastic elastomers with the two types of blocks conforming to the 'soft' and 'hard' segment designations mentioned earlier.

11.1.2.4　Synthesis by oligomer-linking reactions

The simplest variety of oligomer-linking reactions (often termed 'chain extension' reactions) is that in which units of a single type of oligomer, which may be mono- or bi-functional, are connected into a larger molecular chain by means of a bifunctional reactant (equations 5a and 5b). As already noted, it is questionable whether such products are rightly to be regarded as block copolymers.

$$2 P ♦ + ● R ● \longrightarrow P-R-P \tag{5a}$$
$$♦ P ♦ + ● R ● \longrightarrow [-P-R-]_n \tag{5b}$$

In a variation which certainly provides block copolymers, different types of similarly bifunctional oligomers in admixture are linked by a bifunctional co-reactant (equation 6). As with random block copolymer syntheses, this methodology leads to a statistical sequential distribution of the component oligomer units along the chain.

$$♦ P_A ♦ + ♦ P_B ♦ + 2 ● R ● \longrightarrow [-P_A-R-/-P_B-R-]_n \tag{6}$$

The more certain approach leading to products in which the different component species must necessarily alternate along the chain is that involving the combination of two oligomers having mutually reactive end groups such that each species can react only with the other (equation 7). This procedure, which has been used particularly in recent work on polycarbonate–polysulfone and polysiloxane–polysulfone block copolymers, yields multiblock products with structures defined

376　　　　　　　　　　　　　　*Heterochain Block Copolymers*

precisely by those of the starting reactants. As a practical matter, the formation of products of high MW free of contaminating oligomer residues imposes the need for: (1) the prior synthesis of oligomers of high purity with accurately known MW and end group contents; and (2) the means of bringing the oligomers to reaction with the required stoichiometry and in the absence of interfering impurities such as might be contained, for example, in insufficiently purified solvent media.

$$\blacklozenge P_A \blacklozenge \; + \; \bullet P_B \bullet \longrightarrow [-P_A-P_B-]_p \qquad (7)$$

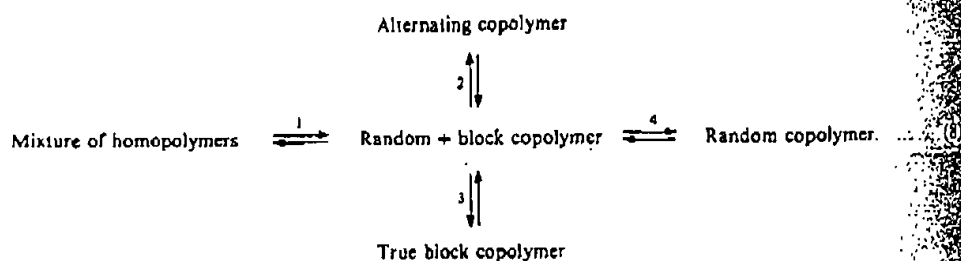### 11.1.2.5　Post reactions of block copolymers

Block copolymers of structures not attainable directly by polymerization reactions can sometimes be prepared by the chemical modification of more readily accessible precursor block polymers. No general principles can be laid down, but examples include: (1) the quaternization of amine group-containing blocks to give polyionic products; (2) the hydrogenation of double bonds in block copolymers derived from dienes, yielding saturated sequences; and (3) the removal of protecting groups in block copolymers to reveal sensitive groups that could not have survived during the construction of the main chain.

11.2　DEVELOPMENTS IN HETEROCHAIN BLOCK COPOLYMER SYNTHESIS

11.2.1　Blockiness in Randomization and Step Copolymerization Reaction Products

Copolymers of partial but imperfectly defined block character are formed by various processes which involve interchange reactions between fissile groups in the main chain structures of non-block precursors. Early examples included the partial inter-randomization of pairs of (homo)polyesters or (homo)polyamides at high temperatures in the melt.[50-55] Such reactions may occur by direct exchange between the relevant groups, or with the involvement of reactive chain end groups or of added catalysts. Analogous rearrangements leading to products in partial block character occur when strictly alternating copolyamides[56,57] or copoly(ester amides)[58,59] are melted, and when polyester–polyamide mixtures are heated in high-boiling solvents.[60] Comparable interchange ('shuffling') reactions can complicate the formation of polysiloxane copolymers, especially in the presence of strongly basic catalysts.[61-63] Interesting examples of the converse process are shown by the behaviour of the random copolyesters poly(cis-co-trans-cyclohexanedimethylene terephthalate) and poly(ethylene terephthalate-co-2-methylsuccinate) which, in critical ranges of temperature shortly below the melting points, undergo transfer of units from the lower-melting component into the crystal lattice of the higher-melting component resulting in conversion to partial block character.[64,65]

Such interchange reactions resemble those leading to the equilibrium of MW's and ring–chain equilibration in many step polymerizations, and are formally interrelated as shown in equation (8). The position of equilibrium in each arm of the scheme is determined by the structures of the substances involved, the mechanistic and thermodynamic pathways available, and the conditions of reaction. The probability of some individual steps may seem indeed to be negligible though the de-randomization reactions mentioned above should make for caution in considering what may be possible. The structure dependence of the processes is illustrated by the relative rates of inter-randomization of some polyesters with 2G.T (step 1), which lie in the order 2G.4 > 2G.6 ≈ 2G.10 > poly(ethylene isophthalate) > poly(ethylene hexahydroterephthalate), whilst with respect to step 3 it has been claimed that block copolymers of 2G.T with sterically hindered aliphatic[66] and aromatic[67] polyesters, and of poly(p-xylylene hexadecamethylenedicarboxamide) with its N,N'-diethyl analogue,[68] are sufficiently stable that they do not undergo randomization in the melt.

Alternating copolymer

$$\Big\updownarrow 2$$

Mixture of homopolymers　$\underset{1}{\rightleftharpoons}$　Random + block copolymer　$\underset{4}{\rightleftharpoons}$　Random copolymer.　　　(8)

$$\Big\updownarrow 3$$

True block copolymer

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·mer　(8)

In general, however, there is an entropy-driven propensity for highly ordered block polymers containing fissile groups to become transformed in suitable conditions into random block copolymers and eventually into wholly random copolymers. Its importance lies in the potential for the loss of structural integrity when such materials are exposed during thermofabrication to temperatures higher than any encountered at earlier stages of their history.

The same considerations apply to blocky heterochain copolymers formed through the preferred reactivity of a particular reactant in an ostensibly random step or condensation polymerization. Typical of such reactions are the co-condensations of: (a) *trans*-2,5-dimethylpiperazine with terephthaloyl chloride and ethylene bis(chloroformate), the first mentioned halide being more reactive;[69] and (b) *cis*-2,6-dimethylpiperazine with terephthaloyl and sebacoyl chlorides, the aromatic dihalide being again the more reactive.[70] In each case, recognition of the reactivity differences permitted the control of experimental procedure by phased introduction of the reactants to yield products of well-developed (though not precisely defined) block character. The course of such reactions may also be influenced by the general parameters of operation as in the solution polycondensation of iso-phthaloyl chloride with mixed *m*- and *p*-phenylene diamines which yields highly blocked copolyam-ide when conducted in tetrahydrofuran but more random copolymers in polar media such as DMAc and HMPA.[71]

Such procedures are nevertheless highly empirical in character and until recently the formation of blocky structures could be inferred qualitatively only from observations of thermal transitions and crystal character, and quantitatively only from simple and often insensitive analyses. For wholly amorphous copolymers, only the latter method was available.

Compositions and sequence distributions in the products of random step copolymerizations (including random block copolymerizations) are important quantities which have been investigated theoretically with the aid of mathematical models.[72-77] However, the relevant kinetic parameters are rarely available to permit valid predictions to be made for the generality of reactions or for variance with practical conditions. The advent of NMR spectroscopy has opened new horizons in the experimental investigation of these problems. In one aspect, it is now often possible to study the competitive enrichment or depletion of a particular component during the course of a polymeriz-ation; in another, the sequences of particular groups may be detected from the chemical shifts shown by specific components of those groups lying in different chemical environments. Thus, if two reactants X and Z of similar type are combined with a common co-reactant Y, the resulting polymer chains will contain the sequences X—Y—X, X—Y—Z (or Z—Y—X) and Z—Y—Z which, if distinguishable by NMR, can be determined and the results expressed in terms of a blockiness parameter B which is the ratio of the measured proportion of the linkages X—Y—Z and Z—Y—X to that expected from Bernoullian statistics for a random copolymer. For a random copolymer $B = 1$, and for an alternating copolymer $B = 2$. Values of $B < 1$ indicate the presence of blocks, with decreasing values of B indicating increasing size of the blocks. In the limiting case, represented by a mixture of homopolymers, $B = 0$.[53,78] The use of this parameter thus permits the investigation of the influence of reaction conditions upon the blockiness of copolymers.

Table 1 shows some problems in heterochain copolymer composition and structure which have been studied by NMR. Other methods which have given useful information include: the use of an isotopically labelled monomer to investigate preferential incorporation during copolymerization;[92] the application of isotopic dilution analysis to polymer degradation products to determine the proportion of isolated units of a particular component;[79] and the use of mass spectrometry to determine blockiness.[93]

11.2.2 Oligomer Synthesis and End Group Refunctionalization Reactions

As outlined previously, many heterochain block copolymer syntheses depend upon the use of preformed oligomeric precursors furnished with suitable reactive end groups. The range of such substances available commercially is limited, consisting essentially of four groups: (a) aliphatic polyethers and copolyethers with hydroxyl (or, in some cases, amino) end groups; (b) hydroxyl-ended aliphatic polyesters and copolyesters; (c) hydroxyl-ended polybutadienes; and (d) poly siloxanes. For research purposes other types of oligomers have been made by condensation reactions, using a deficit of one reactant to afford, for example, polyamides, polycarbonates and polysulfones with required end groups; examples of these will appear in later sections. Considerable use has also been made of the living polymerizations of styrene and dienes where, by suitable termination reactions carbochain oligomers are obtained with end groups that can take part in subsequent condensation or other block-forming linking steps. Prominent amongst these are the

378　　　　　　　　　　　　　　　　*Heterochain Block Copolymers*

Table 1　Some NMR Studies of Heterochain Copolymer Composition and Structure

Substance or System Investigated	Method and Feature Studied	Ref.
Inter-randomization of 2G,T and 2G,10 polyesters	^{1}H NMR in F_3CCO_2H at 70°C for determination of T-2G-T, T-2G-10 and 10-2G-10 sequences	53
Piperazine group-containing copolyamides and polyurethanes	^{13}C NMR using CO group resonances to study composition, chemical stability and cisoid-transoid isomerism	57
De-randomization of 2G,T–poly(ethylene 2-methylsuccinate) random copolymers	^{1}H NMR in F_3CCO_2H at 37°C using $O(CH_2)_2O$ protons for determination of sequence lengths	65
Condensation of isophthaloyl chloride with mixed m- and p-phenylenediamines and of m-phenylenediamine with mixed iso- and tere-phthaloyl chlorides	^{1}H NMR in DMAc-LiCl using amide group proton resonances to determine blockiness	71
Copolymers from iso- or tere-phthaloyl chlorides with 2,2-dimethyl-1,3-propanediol and bisphenol A made in various conditions	^{1}H NMR in $CDCl_3$ for determination of sequence lengths	77
Copolymers from isophthaloyl chloride and $O[PhNH_2]_2 + SO_2[PhNH_2]_2$ made in different solvent media	^{1}H NMR in DMAc-LiCl at 80°C for determination of sulfone → sulfone, sulfone → ether, ether → sulfone and ether → ether unions	78
Solution and interfacial condensation of $COCl_2$ + benzene-m-disulfonyl chloride with bisphenol A	^{13}C NMR in $CDCl_3$ at 60°C, using methyl resonances to determine carbonate → carbonate, sulfonate → carbonate and sulfonate → sulfonate linkages	79
Poly(m-phenyleneisophthalamide)-block-poly(oxyethylene) and poly(m-phenyleneisophthalamide)-block-poly(dimethylsiloxane) Poly[BPPAC-block-poly(dimethylsiloxane)]	^{1}H NMR determination of aromatic proton:aliphatic ether and aromatic proton:siloxane methyl protons to confirm composition	80
	^{13}C and ^{29}Si NMR using $(acac)_3Cr$ shift reagent for complete analysis of composition and microstructure	81
Block polymers from H_2NPh-$PhNH_2$ with adipoyl and terephthaloyl chlorides	^{1}H NMR in $ClSO_3H$ for determination of terephthaloyl group content	82
Solution copolymerization of terephthaloyl chloride (T) with bisphenol A (B) and 4,4'-dihydroxy-1,1'-binaphthyl (N)	^{1}H NMR in $C_2H_2Cl_4$ at 140°C for determination of N–T–N, N–T–B and B–T–B sequences in relation to B:N ratio	83–85
Polyamide from $H_2N(CH_2)_2NH_2$ and $ClCOPhCH_2SCH_2COCl$ made in various conditions	^{1}H NMR in DMSO at 120–134°C to determine head–head, head–tail, tail–tail combination sequences	86
Anionic copolymers from ε-caprolactam and α-caprylactam with γ-butyrolactam	^{13}C NMR in FSO_3H using CO group signals to determine composition and sequencing	87
Various aliphatic, alicyclic and aromatic copolyesters	^{13}C NMR in F_3CCO_2H using CO and OCH_2 group signals to distinguish copolymers from mixed homopolymers and determine lengths of homogeneous blocks	88
Ternary polyester amides with alternating sequences of aminobenzoyl, glycyl and hydroxy- or mercapto-acetyl residues	^{1}H NMR in F_3CCO_2H to confirm sequence patterns	89
2G,T-block-poly(oxyethylene) random block copolymers	^{13}C NMR in $CDCl_3$ for determination of average composition and degradation of POE units during polymerization	90
2G,T-co-4G,T	^{13}C and ^{1}H NMR to determine blockiness and formation of oxydiethylene groups by side reactions of polymerization	91

2-hydroxyethyl-ended oligomers formed by treatment of the oligomer carbanions with oxirane (ethylene oxide). Their preparations depend upon the fact that at relatively low temperatures the carbanion P^- is capable of opening the oxirane ring to give $P—CH_2CH_2O^-$ which is insufficiently reactive in these conditions to initiate polymerization of further oxirane molecules, though it can do so at higher temperatures.[94-97] Thus, by control of reaction temperature and nature of the counterion,[98,99] a single oxyethyl anion group can be attached at the reactive chain end(s) and converted to hydroxyethyl by treatment with a source of protons. In practice, the procedure is affected by a troublesome increase in viscosity at the oxyanion stage and is limited by the restricted solubility of many organolithium initiators (particularly dilithio initiators for bifunctional polymerization) in hydrocarbon reaction media. Attempts at the amelioration of these difficulties include the use of soluble lithium-ended low MW polydienes as initiators for butadiene polymerization,[100] of phenyloxirane as the source of oxyanions,[101] and of 6-tetrahydropyranyloxy- or 6-[1-ethoxy-(ethoxy)]-hexyllithium as the initiator for butadiene polymerization to give products reactable with oxirane at one end of the polydiene molecule, whilst carrying an acetal group at the other from which hydroxyl can finally be released by hydrolysis.[102]

The complex nature of these procedures, and the variable success obtained in other carbanion reactions (*e.g.* the sequence $P^- \xrightarrow{CO_2} PCO_2^- \xrightarrow{H^-} PCO_2H$) has encouraged work towards alternative methods for the synthesis of useful reactive oligomers from readily accessible starting materials. Such approaches commencing with dienes include free radical polymerizations initiated by 4,4'-azobis(4-cyano-1-pentanol) or 4,4'-azobis(4-cyanopentanoic acid) giving polydiene oligomers terminated with OH and CO_2H groups respectively;[103-105] with living anionic polystyrene or polydienes, by direct oxygenation to α,ω-bis(hydroperoxy) oligomers which can be reduced to diols,[106,107] and with butadiene by polymerization with H_2O_2–$HClO_4$ or by redox telomeriz-ation.[108,109] Styrene has also been oligomerized by $AlCl_3$–$SOCl_2$ to α,ω-dichloropolystyrenes which can be converted to α,ω-diamines and diols.[110] A novel development makes use of the termination-free polymerization of isobutene initiated by α,α'-dichloro-1,4-diisopropylbenzene + BCl_3 which gives rise to oligomers having 1-chloro-1,1-dimethylethyl end groups (equation 9). These products can be converted by way of dehydrochlorination and subsequent hydroboration to polyisobutenes having primary hydroxyl end groups (equation 10).[111]

$$ClMe_2CPhCMe_2Cl \; + \; (2n \; + \; 2)C_4H_8 \xrightarrow{BCl_3}$$

$$ClCMe_2—CH_2[CMe_2CH_2]_n—CMe_2PhCMe_2—[CH_2CMe_2]_n—CH_2CMe_2Cl \tag{9}$$

$$P—CH_2CMe_2Cl \xrightarrow[\text{in THF}]{KOBu^t} P—CH_2CMe=CH_2 \xrightarrow[\text{(ii) NaOH/H}_2O_2]{\text{(i) 9-BBN}^* \text{ in THF}} P—CH_2CHMeCH_2OH \tag{10}$$

* 9-borabicyclo-3,3,1-nonane

Mention may also be made of the controlled ozonolytic or oxidative degradations of high MW isotactic poly(oxypropylene),[112] poly(vinyl chloride),[113] and poly(isobutene-*co*-2,3-dimethylbuta-diene)[114] to give oligomers with functional end groups. However, no effective synthesis has yet been devised for α,ω-difunctional polymethylene oligomers which would be of considerable interest as precursors of block copolymers.

Much effort has also been given to extending the range of block-forming reactions of accessible oligomers by refunctionalization of their end groups. Familiar examples include the transformations of hydroxyl-ended oligomers P—OH (only one end group is shown, though the materials are often bifunctional) with diisocyanates,[15,115-118] phosgene[95,97,117,119,120] or dicarbonyl chlorides[90,96,121-124] to give P—OCONHRNCO, P—OCOCl and P—OCORCOCl, respectively. Table 2 shows further refunctionalization reactions and reaction sequences which have been explored in recent years; additional instances will be mentioned in later sections in connection with the synthesis of particular classes of block polymers.

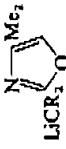### 11.2.3 Polyether and Polythioether Block Copolymers

The ring-opening polymerization of oxirane initiated by terminally mono- or di-carbanionic carbochain oligomers provides a direct route to AB and BAB block copolymers [where A represents the carbochain entity and B is poly(oxyethylene)]. Substances which have been prepared in this

380　　　　　　　　　　　　　　　*Heterochain Block Copolymers*

Table 2　Refunctionalization Reactions of Oligomers

Refunctionalization Agent(s)	Oligomer Product	For Reaction With	Ref.
Polymer carbanion (P⁻)	1. CO_2, H⁺ 2. Esterify 3. $LiAlH_4$	P—CH_2OH	OH, NCO	15
Polymer carbanion (P⁻)	cyclo-[$SiMe_2$O]₃	P—$SiMe_2$O⁻	Cyclopolysiloxanes (polymerization)	125
Polymer carbanion (P⁻)	BrCH_2CH—CH_2 (epoxide)	P—CH_2CH—CH_2 (epoxide)	NH_3	126
Polymer carbanion (P⁻)	1. CO_2, H⁺ 2. $SOCl_2$ 3. $H_2N(CH_2)_x NH_2$	P—CONH$(CH_2)_x NH_2$	Oxazolidin-2,5-diones (polymerization)	127, 128
Polymer carbanion (P⁻)	1. $MgBr_2$ 2. Br_2 3. $AgClO_4$	P⁺ClO_4^-	Tetrahydrofuran (polymerization)	129
Polymer carbanion (P⁻)	1. CO_2, H⁺, $SOCl_2$ 2. $AgClO_4$	P—CO⁺ClO_4^-	Cationically polymerizable monomers	130
Polymer carbanion (P⁻)	1. MeCN 2. $LiAlH_4$/THF	P—CHMeNH_2		131
Polymer carbanion (P⁻)	1. CO_2, H⁺ 2. Bu_4NOH	P—CO_2^- ⁺NBu_4	Pivalolactone (polymerization)	132
P—OH	1. R(NCO)₂ 2. Glycidol	P—OCONHRNHCO₂$CH_2$$CH_2$CH—$CH_2$ (epoxide)	NH_3	134

Heterochain Block Copolymers　　　　381

Substrate	Reagents	Product		Reference
Polymer carbanion (P⁻)	1. CO_2, H^+ 2. Bu_4NOH	$P-CO_2^-\ {}^+NBu_4$	Pivalolactone (polymerization)	132
Polymer carbanion (P⁻)	$ClCO_2Et$	$P-CO_2Et$		133
P—OH	1. $R(NCO)_2$ 2. Glycidol	$P-OCONHRNHCO_2CH_2CH\!-\!CH_2$ (epoxide)	NH_3	134
P—OH	$OCNCH_2CH=CH_2$	$P-OCONHCH_2CH=CH_2$	Hydrosilanes	135, 136
P—CH_2CH_2OH	$MePhSO_2Cl$, pyridine	$P-CH_2CH_2OSO_2PhMe$	1. 2-Oxazolines (polymerization) 2. $PhCH_2NH_2$, giving $P-NHCH_2Ph$	137, 138
P—OH	1. $ClCOPhNO_2$, pyridine 2. $H_2/Pd/C$	$P-OCOPhNH_2$		139
P—OH	1. $OCN(CH_2)_6NCO$ 2. HCl/H_2O	$P-OCONH(CH_2)_6NH_2$		131
P—$(CH_2)_4Br$	1. [N-Me_2 furan ring] $LiCR_2$ 2. H^+/H_2O	$P-(CH_2)_4CR_2CO_2H$	As Bu_4N^+ salt for polymerization of pivalolactone	140
P—OH	Succinic anhydride	$P-OCO(CH_2)_3CO_2H$	As Bu_4N^+ salt for polymerization of pivalolactone	141–143
P—NH_2	1. $R(NCO)_2$ 2. Glycidol	$P-NHCONHRNHCO_2CH_2CH\!-\!CH_2$ (epoxide)	NH_2	157

way include those with A units of polystyrene,[94,95,98,144] poly(ethyl methacrylate),[145] poly-(2-vinylpyridine),[146] polydienes,[147,148] and preformed triblock isoprene–styrene copolymers.[149] A variation leading to three-armed A(B)$_2$ block copolymers has been achieved by attaching the 2-naphthylmethylene group at the ends of polystyryl or poly(4-*t*-butylstyryl) chains followed by metallation with potassium to generate dianions (13) having two reactive sites available for initiating the growth of POE chains.[150]
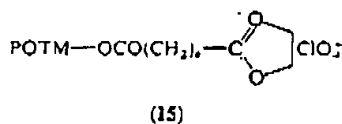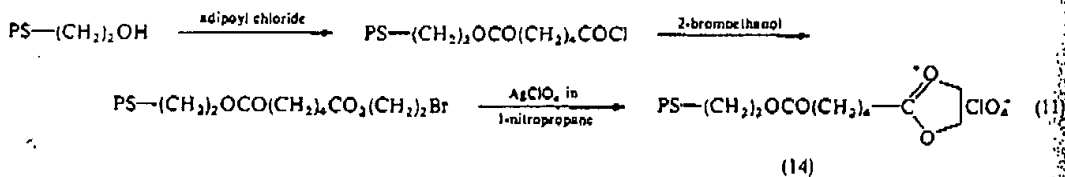

(13)

The approach cannot ordinarily yield ABA copolymers because poly(oxyethylene)oxy anions are unable to activate most vinyl monomers for sequential polymerization. However, in the presence of a strong base complexed with crown ether or cryptate ligands, POE chains with NHCH$_2$Ph or OH end groups become sufficiently nucleophilic to initiate the polymerization of methyl and *t*-butyl methacrylates giving triblock polymers with central POE segments.[138,151]
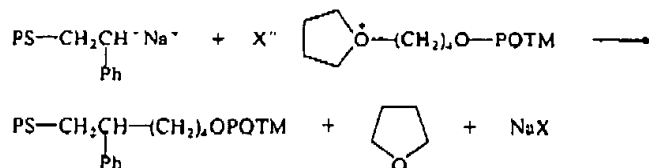
Tetrahydrofuran cannot be polymerized by bases and the living anionic principle is therefore not available for the formation of block polymers with poly(oxytetramethylene) segments. Recent work, mostly involving cationic intermediates, has provided the following approaches to the synthesis of POTM-containing block copolymers.

(a) Polystyrenes with COCl end groups, when treated with silver salts such as AgBF$_4$, AgSbF$_6$ or AgClO$_4$ having anions of low nucleophilicity, are converted to oxocarbenium (acylium) species (PS—CO$^+$) which can initiate the polymerization of THF and other cation-sensitive monomers.[130]

(b) By the sequence of reactions shown in equation (11), 2-hydroxyethyl-ended polystyrene is converted to (14) whose terminal dioxolenium group is used to initiate the polymerization of THF to a PS—POTM block copolymer. Analogous reactions lead to the dioxolenium-ended POTM (15) which can initiate the polymerization of 3,3-bis(chloromethyl)oxetane and of 7-oxabicyclo[2.2.1]-heptane yielding block copolyethers.[96]

(14)

(15)

(c) The transfer-free polymerization of THF initiated by AgClO$_4$ + 2-bromoethyl acetate or bis(2-bromoethyl) sebacate, or by AgPF$_6$ + benzyl bromide or *m*-xylylene dibromide gives POTM structures with cyclic oxonium groups at one or both ends of the molecule according to the functionality of the halide used. These active end groups react with carbanionic polystyrenes as shown in equation (12) forming POTM block copolymers.[152–6]
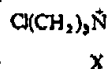

(12)

(d) By reaction with AgClO$_4$, the terminal halogen atom of ω-bromopolystyrene, or preferably the *m*-xylylene homologue (16) which is not prone to hydrohalide elimination, is converted to a corresponding carbenium perchlorate, e.g. (14), which combines with a single THF molecule at low

temperatures forming an oxonium complex (18) that can initiate the polymerization of THF at higher temperatures to form block copolymers (equation 13).[129,158]

$$PS-CH_2CHCH_2-m\text{-}Ph-CH_2Br \xrightarrow{A_8ClO_4} PS-CH_2CHCH_2-m\text{-}Ph-CH_2^+ClO_4^- \xrightarrow{THF}$$
$$\underset{Ph}{|} \qquad\qquad\qquad\qquad \underset{Ph}{|}$$
(16) (17)

$$PS-CH_2CHCH_2-m\text{-}Ph-CH_2-\overset{+}{O}\bigcirc ClO_4^- \qquad (13)$$
$$\underset{Ph}{|}$$
(18)

(e) The polymerization of THF initiated by trifluoromethanesulfonic anhydride gives the dicationic polymer (19) whose end groups can be displaced by 1,4,4-trimethylazetidine yielding (20) which then serves as an initiator for polymerization of the cyclic amine to polyether–polyamine triblock copolymers (21).[33]

(19) 2CF₃SO₃⁻

(20) 2CF₃SO₃⁻

(21) 2CF₃SO₃⁻

(f) α,ω-Dibromopolyethers (including POTM), formed by reaction of the α,ω-diols with thionyl bromide, are linked by quaternization with tertiary amine-ended ionene oligomers to give polyionic block copolymers (22) with central polyether segments (equation 14).[34,159]

$$2Cl(CH_2)_3\overset{+}{N}Me_2[(CH_2)_3\overset{+}{N}Me_2]_n-(CH_2)_3NMe_2 + Br[(CH_2)_4O]_n-(CH_2)_4Br \longrightarrow$$
$$\quad X^- \qquad\qquad X^-$$

$$Cl(CH_2)_3\overset{+}{N}Me_2[(CH_2)_3\overset{+}{N}Me_2]_n-(CH_2)_3\overset{+}{N}Me_2-[(CH_2)_4O]_n-(CH_2)_4-\overset{+}{N}Me_2(CH_2)_3[Me_2\overset{+}{N}(CH_2)_3]_n\overset{+}{N}Me_2(CH_2)_3Cl$$
$$\quad X^- \qquad\qquad X^- \qquad\qquad Br^- \qquad\qquad\qquad Br^- \qquad\qquad X^- \qquad (14)$$
(22)

Free radical polymerization has been employed for syntheses of some POE block copolymers. In one approach, POE chains with peroxycarbamate[118] or *t*-butyldioxycarbonylbenzoate[160] end groups were used to initiate block polymerizations with styrene. Hydrophilic poly(2-hydroxyethyl methacrylate)–POE block copolymers have been made by radical polymerization of the meth-acrylate with 2-aminoethanethiol as chain transfer agent, giving amino-ended oligomers which were coupled to the polyether by reaction with a diisocyanate.[161] Free radical intermediates may also be involved in the primary stages of the complex reaction leading to the formation of block copoly(arylene ether)s when 2,6-diphenylphenol is co-oxidized with 2,6-dimethylphenol or 2-methyl-6-phenylphenol using oxygen and Cu(I)/amine catalysts.[162] In general, however, free radical reactions do not offer versatile and controllable means for the synthesis of structurally well-defined block copolymers.

Lastly, mention will be made of some methods for the formation of block copolymers containing poly(thioalkylene) sequences by the ring opening polymerizations of cyclic sulfides.

In anionic systems, thiiranes and thietanes undergo ring opening by different pathways, involving thiolate intermediates in the first case (equation 15) and carbanions in the second (equation 16).

384   *Heterochain Block Copolymers*
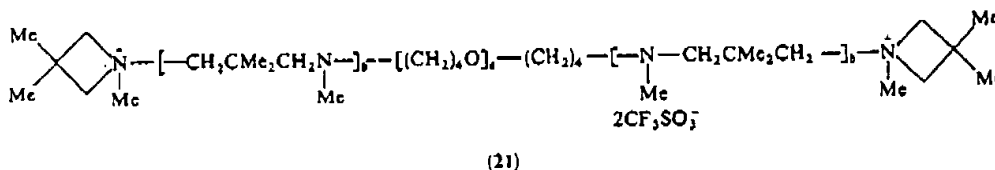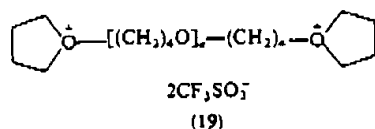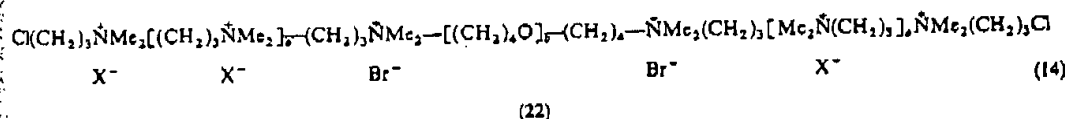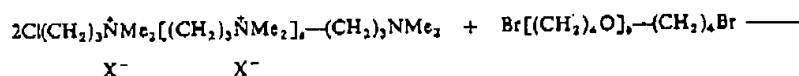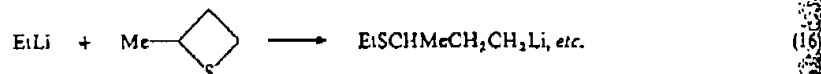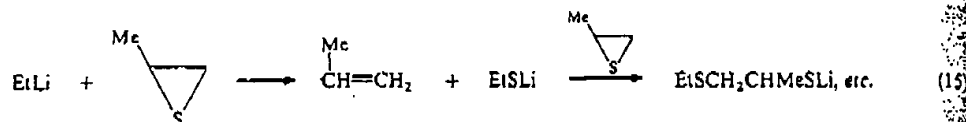
$$EtLi + \triangle\!\!-\!\!S\,(Me) \longrightarrow CH{=}CH_2 + EtSLi \longrightarrow \triangle\!\!-\!\!S\,(Me) \longrightarrow EtSCH_2CHMeSLi, etc. \qquad (15)$$

$$EtLi + Me\!-\!\square\!-\!S \longrightarrow EtSCHMeCH_2CH_2Li, etc. \qquad (16)$$

The blockwise polymerization of either type of monomer can be induced by polyvinyl or polydienyl anions (A) to give AB or BAB copolymers, where B represents the poly(thioalkylene) sequences. In the thiirane case, the thiolate end group of the AB copolymer can readily be coupled with phosgene to give $A(B)_2A$ copolymers, whilst with thietanes the terminal carbanionic group can be used to initiate polymerization of vinyl monomers to give ABA or ABC block copolymers.[163,164] Block copolymers of methylthiirane with thiirane or with 2,2-dimethylthiirane have also been obtained by sequential polymerizations initiated in the first phase by 2-naphthylsulfonylmethylene anions.[165] Cationic polymerization has found use in the conversion of 3,3-dimethylthietane to SH ended oligomers which could be coupled with hydroxyl-ended POE chains by reaction with a diisocyanate,[166] but attempts to obtain block polymers of this thietane by direct initiation with cationic polystyrene were not successful.[167]

11.2.4 Polyester Block Copolymers

Apart from copoly(ester urethane)s, synthetic developments towards polymers containing poly ester blocks have been dominated by two main themes, the first stemming from early work on block poly(ether ester)s and the second from interests in the ring-opening polymerization reactions of cyclic esters (lactones).

Polymers of the first group are typified by the poly(alkylene terephthalate)–poly[poly(oxy alkylene) terephthalate] family which are conveniently prepared by the copolyesterification of dimethyl terephthalate with mixtures of a short-chain diol and a poly(oxyalkylene)-α,ω-diol according to the general scheme of equation (3).[7,8,90,168-175] Many different diols, polyether diols and aromatic dicarboxylate esters other than terephthalates have been employed in such investigations,[171,174-176] and a generalized view of the properties attainable is shown in Figure 3.
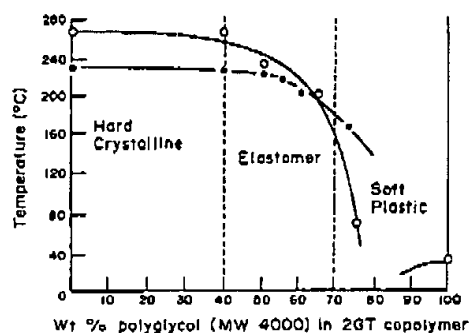

Figure 3 Properties *vs.* composition relationships for polyether–poly(ethylene terephthalate) random block copolymers. O, crystalline melting point (by X-ray); ●, polymer melt temperature (reproduced from W. H. Church and J. C. Shivers, *Text. Res. J.*, 1959, 29, 538 with permission of the Textile Research Institute)

Because of their hydrophilic nature the 2G.T–POE group of block copolymers are unsuitable for use as structural substances but this very property has indicated their application as electrostatic charge dispersants in synthetic fibres[177] and as potentially useful biodegradable surgical materials.[90] Most attention has been devoted to the thermoplastic elastomeric group of random block poly(ether ester)s, notably those based on 4G.T (or 4G.T-*co*-isophthalate) as the hard block components and POTM terephthalate as the soft segments which have emerged as important commercial products. These copolymers combine ready processability with excellent mechanical

properties that are sustained over a wide temperature range (-55 to $+150$ °C), and with good resistance to many oils and chemicals. The optimum MW of the POTM component is approximately 1000, and variations in the hard segment content over the range 30–80 wt % gives copolymers of correspondingly increasing hardnesses and moduli, reflecting a progressive change from soft elastomeric to tough elastoplastic character. The scientific and technological properties of these materials are detailed in a number of publications[171,174,175,178-192] and are discussed fully in ref. 312. Since their commercial début in the early 1970s, the annual US consumption has risen to 7000 tons.[193]

Elastomeric polymers with poly(arylene carbonate) hard blocks (23) have been made according to equation (17) by the co-phosgenation of bisphenols with soft segment oligomer α,ω-diols in the presence of an acceptor for the liberated hydrogen chloride.[194-196] Since these reactions take place at relatively low temperatures where structural reorganization by ester–ester exchange does not occur, aliphatic polyester diols can be employed to give poly(arylene carbonate)–aliphatic polyester block copolymers. Bisphenols which have been used in such preparations include bisphenol-A (4,4'-(1-methylethylidene)bisphenol), and the hindered compounds (24) and (25) which give amorphous hard bloc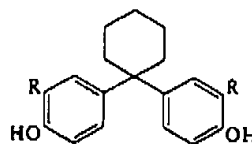ks. Other procedures giving polyester–polyester or polyester–polyether block polymers are: (a) the condensation of hydroxyl-ended with chloroformate-ended oligomers;[197-201] and (b) the coupling of hydroxy-ended oligomers by means of dicarbonyl chlorides, diisocyanates or dichlorodimethylsilane.[202-205]

$$aHOArOH \ + \ bHO{-}P{-}OH \ + \ (a \ + \ b)COCl_2 \ \longrightarrow \ [{-}({-}OArOCO{-})_a{-}({-}OPOCO{-})_b{-}]_x \quad (17)$$
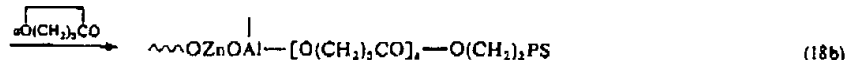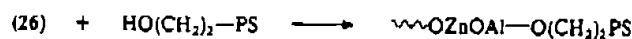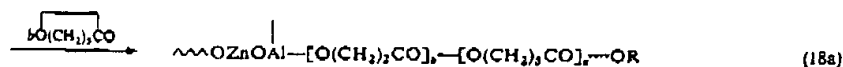
<div align="center">(23)</div>

(24)　　　　　　(25) R = R = H or Me

The ionically initiated ring-opening polymerization reactions of lactones[206] should be adaptable in principle to the formation of block polymers. In practice such reactions are complicated by the unequal propensities of different lactones for polymerization and by the occurrence of interchange side reactions catalyzed by the ionic species present. Binary copolyesters of partial block character are formed in some lactone–lactone copolymerizations carried to limited conversions,[92,207] but attempts to prepare block copolymers by the reactions of lactones with preformed polyvinyl, polydienyl or poly(oxyalkylene) anions have generally been unsatisfactory because of the considerable concurrent formation of higher cyclic polyester oligomers and of free homopolymers of the initiating species.[208-210] These difficulties, which may reflect the effects of proton abstraction from the active α-methylene position in the lactone or its derived polyester chain, can be avoided in the case of polyhydrocarbon anions by end-capping with oxirane before introduction of the lactone, and such modifications have permitted the formation of polystyrene-*block*-polybutadiene-*block*-poly(ε-caprolactone) triblock polymers.[211-213]

A novel approach to the synthesis of block copolymers from lactones involves coordination catalysis by bimetallic oxoalkoxides which, in quite mild conditions, polymerize cyclic esters by insertion at the Al—OR bond of the catalytic complex (26). The sequential introduction of different

$$\sim\sim OZnOAl{-}OR \xrightarrow{aO(CH_2)_3CO} \sim\sim OZnOAl{-}[O(CH_2)_3CO]_aOR$$

<div align="center">(26)</div>

$$\xrightarrow{bO(CH_2)_5CO} \sim\sim OZnOAl{-}[O(CH_2)_5CO]_b{-}[O(CH_2)_3CO]_a{-}OR \quad (18a)$$

$$(26) \ + \ HO(CH_2)_2{-}PS \ \longrightarrow \ \sim\sim OZnOAl{-}O(CH_2)_2PS$$

$$\xrightarrow{aO(CH_2)_3CO} \sim\sim OZnOAl{-}[O(CH_2)_3CO]_a{-}O(CH_2)_2PS \quad (18b)$$

lactones leads to polyester–polyester block polymers as shown in equation (18a), and the prior attachment of polystyryl unit (as alkoxide) to the aluminum atom opens an elegant route to polystyrene-*block*-poly(ε-caprolactone) block copolymers (equation 18b).[214-217]

A further effective approach to lactone-based block copolymers makes use of the specific ability of α,α-dialkyl-β-propiolactones (3,3-dialkyloxetan-2-ones) to undergo living anionic polymerizations initiated by tetraalkylammonium carboxylate salts and propagated, through an alkyl–oxygen fission mechanism, by carboxylate anions. Much attention has been devoted to the case of pivalolactone (3,3-dimethyloxetan-2-one) (27) on account of the high-melting crystalline character of its polymer which, as a hard segment component in elastomeric block copolymers, provides a system of thermally reversible quasi-crosslinks. The general form of the reaction is shown in equation (19), and equation (20) (in which the ammonium counterions are omitted for simplicity) shows examples of its adaptation to the formation of various types of block copolymers.[218-221] The effectiveness of the initiating step (and hence the possibility of achieving sequential polymerization) is affected by the proximity of the initiating carboxylate anion to other polar groups;[141] nevertheless, within certain limitations, the method provides a valuable source not only of the block copolymer types shown above but also of thermoplastic graft copolymers having poly(pivalolactone) branches attached to carbochain polymer backbones by reaction at pendant CO_2H groups.[218,222-225]

11.2.5 Polyamide, Polypeptide and Related Block Copolymers

It has long been known that the properties of partially *N*-alkylated linear polyamides vary with the pattern of distribution of the substituent groups, *i.e.* with the degree of randomness or blockiness of the unsubstituted and the substituted amide groups along the chain.[8,68,226-228] Indeed such polymers formed an early focus of interest in the development of non-hydrocarbon elastomers though they were soon overtaken in importance by the elastomeric block copolyurethanes which retain a similar dependence upon hydrogen bonding as the effective source of high-melting and cohesive character in their hard segments whilst being more readily and controllably prepared. Block copolymers containing polyamide or similar segments will here be considered as a class.

Adventitious routes to partially blocky copolyamides have been mentioned in an earlier section, and block copolymer syntheses by conventional random block copolymerization and by oligomer combination reactions are summarized in Tables 3 and 4. It should be noted that the high melting points and restricted solubilities which are the source of useful properties in intermolecularly hydrogen-bonded polyamides and analogous polymers are also a frequent source of practical difficulties in the preparation of their block copolymers.

The activated anionic polymerization of cyclic amides (lactams) offers another recently employed approach to the synthesis of block polymers with polyamide segments. The mechanism of the

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(20b)

$2n\,(27)$

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Table 3　Polyamide and Similar Block Polymers by Random Block Polymerization Reactions

Oligomeric reactant[a]	Coreactant(s)	Product Type	Ref.
$ClCO\text{-}m\text{-}PhCO_2[POE]OCO\text{-}m\text{-}PhCOCl$	$m\text{-}Ph(NH_2)_3 + m\text{-}Ph(COCl)_2$	Polyether-*block*-polyamide	80
$H_2N[PS]NH_2$	Nylon 6,6 salt	Polystyrene-*block*-polyamide	110
$ClCO(CH_2)_4CO[2G.T]O(CH_2)_4OCO(CH_2)_4COCl$	$H_2N(CH_2)_6NH_2 + ClCO(CH_2)_4COCl$	Polyester-*block*-polyamide	123
$HO[POTM]OH$	$MeO_2CPhCONH(CH_2)_4NHCOPhCO_2Me + HO(CH_2)_4OH$	Polyether-*block*-poly(ester amide)	176
$ClCO[O(CH_2)_3CO]_xO[(CH_2)_6O[CO(CH_2)_3O]_xCOCl$	$H_2N(CH_2)_6NH_2 + ClCO(CH_2)_4COCl$	Polyester-*block*-polyamide	260
$HO[POE]OH$	$Ar(CO_2H)_2 + HO(CH_2)_2NH_2$	Polyether-*block*-poly(ester amide)	230
$HO_2C[POE]CO_2H$	Methylhexamethylenediamines $+ EtO_2CCO_2Et$	Polyether-*block*-polyoxamide	231
$H_2N(CH_2)_3[POE](CH_2)_3NH_2$	$HO_2C(CH_2)_4CO_2H + $ aliphatic diamine or piperazine	Polyether-*block*-polyamide	232
$\begin{array}{c} Bu^i \qquad\qquad Bu^i \\[2pt] Et \qquad\qquad Et \\[2pt] HN(CH_2)_6NH[CO(CH_2)_4CON(CH_2)_6N{-}]_nH \end{array}$	2,5-Dimethylpiperazine $+ ClCOPhCOCl$	Polyamide-*block*-polyamide	232
$ClCO_2(CH_2)_2OCO[N(CH_2)_6NCO_3(CH_2)_2O]_nCOCl$	Piperazine $+ m\text{-}Ph(OCOCl)_2$	Polyurethane-*block*-polyurethane	233
$HO[POE]OH$	Nylon 6,10 salt	Polyether-*block*-polyamide	234
$H_3\overset{+}{N}(CH_2)_3[POE](CH_2)_3\overset{+}{N}H_3^-O_2C(CH_2)_4CO_2^-$	ε-Caprolactam	Polyether-*block*-polyamide	235
PS^-, PBd^- or $PS\text{-}block\text{-}PBd^-$	TDI $+ m\text{-}Ph(NH_2)_2$ (directly, or by intermediate reaction with water)	Polyhydrocarbon-*block*-polyurea	236–239
$HO[POTM]OH$	Laurolactam $+ HO_2C(CH_2)_{10}CO_2H$	Polyether-*block*-polyamide	240

[a] Symbols such as $HO[POE]OH$ indicate an α,ω-difunctional oligomer (see Section 11.I.1 for comment on the nomenclature and designation of such substances).

Table 4　Block and Segmented Polyamides and Related Polymers by Oligomer Combination Reactions*

Oligomer A	Oligomer B or Other Coreactant	Product Type	Ref.
H[NHCH$_2$PhCH$_2$NHCO(CH$_2$)$_{16}$CO]$_n$NHCH$_2$PhCH$_2$NH$_2$	HO$_2$C(CH$_2$)$_{16}$CO[NCH$_2$PhCH$_2$NCO(CH$_2$)$_{16}$CO]$_n$OH (with Et substituents)	Polyamide-*block*-polyamide	68
Cl[CO-*m*-PhCONH-*m*-PhNH]$_n$CO-*m*-PhCOCl	HO[POE]OH	Polyether-*block*-polyamide	80
ClCO(CH$_2$)$_4$CO[POE]OCO(CH$_2$)$_4$COCl	H$_2$N(CH$_2$)$_6$NH$_2$, aqueous NaOH	Segmented poly(ether amide)	124
(epoxide)CH$_2$O[PS]OCH$_3$	H[NH(CH$_2$)$_3$CO]$_3$—NH(CH$_2$)$_6$NH—[CO(CH$_2$)$_3$NH]$_3$H	Polystyrene-*block*-polyamide	126
H$_2$NPhCO$_2$[POE]OCOPhNH$_2$	Pyromellitic dianhydride	Segmented poly(ether imide)	139
OCNPhCO$_2$[POP]OCONHPhCH$_2$PhNCO	Pyromellitic dianhydride	Segmented poly(ether urethane imide)	241
OSNPhOPhCONHPhOPhNHCOPhOPhNSO	Water + *m*-Ph(COCl)$_2$	Segmented polyamide	242
(piperidine)HN—[CO$_2$(CH$_2$)$_4$OCON(piperidine)N—]$_n$H	ClCO$_2$[POTM]OCOCl	Polyether-*block*-polyurethane	243
HO$_2$C(CH$_2$)$_4$CO[NH(CH$_2$)$_6$NHCO(CH$_2$)$_4$CO]$_n$OH	H[O(CH$_2$)$_2$OCOPhCO]$_n$O(CH$_2$)$_2$OH	Polyester-*block*-polyamide	244
(imide/piperidine structure) H[NHPhCH$_2$PhNH]$_n$ ...NCO(CH$_2$)$_4$CO...	ClCO[PBd]COCl	Polybutadiene-*block*-poly(amide imide)	245
(piperidine structure)	Cl[COPhCON—(piperidine)—COPhCOCl]$_n$	Polyamide-*block*-polyamide	246
Nylon 11 oligomers with one or two CO$_2$H, or two ester end groups	[POE] and [POTM] with one or two OH end groups	Polyether-*block*-polyamide	247
Various homo- and co-polyamides with two NH$_2$ end groups	OCN(CH$_2$)$_6$NHCO[POE]O[POE]O$_2$CNH(CH$_2$)$_6$NCO	Urea-linked polyether-*block*-polyamide	248

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reaction is complex (for an account of the chemistry see ref. 206) but its overall result is shown in equation (21) where the compound (28) (with R = alkyl, aryl or RNH) is an N-acyl or N-carbamoyl lactam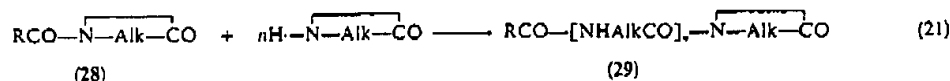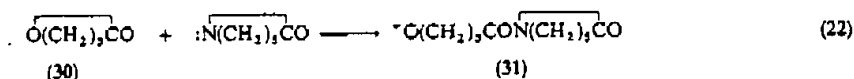 which is used in catalytic quantities as the activator of polymerization together with a catalytic amount of an initiating base (*e.g.* NaH) which generates anions from the lactam monomer, these being the effective intermediates of reaction.

$$\text{RCO—N—Alk—CO} \ + \ n\text{H.—N—Alk—CO} \longrightarrow \text{RCO—[NHAlkCO]}_n\text{—N—Alk—CO} \qquad (21)$$
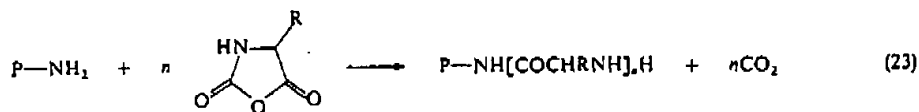
$$(28) \hspace{5cm} (29)$$

Evidently, if R is polymeric the product (29) will be a block copolymer, of AB or ABA type according to the functionality of the activator. For the reaction to proceed satisfactorily the ring $\rightleftharpoons$ chain equilibrium between lactam and polyamide must be favourable for polymerization in the conditions employed, and there must be an absence of side reactions causing loss of propagative anionicity or transfer leading to the formation of free lactam homopolymer. Successful polymerizations have been achieved giving products with polyether,[249,250] polystyrene[133,251-253] SBR,[250] polydiene[133,251] or polyisobutene[254] blocks, usually in combination with nylon 6 as the polyamide segment(s) or, in some cases, with nylon 4 or nylon 8.

Polybutadiene-*block*-nylon-6 copolymers prepared in this way are curable with dicumyl peroxide to hard resins of good flexural strength and impact resistance.[255]

The reaction cannot be extended to the formation of well-defined polyester–polyamide block copolymers. Thus, ε-caprolactone (2-oxepanone) (30) is an effective precursor (by combination with lactamate anion) of an acyllactam activator (31) for the polymerization of ε-caprolactam (hexahydro-2H-azepin-2-one) (equation 22), and this activator might be expected to initiate the polymerization of further lactone molecules from its oxyanion end concurrently with that of lactam from the cyclic end, to give AB poly(caprolactone)–poly(caprolactam) block polymers. Under initiation by strong base the two monomers are indeed copolymerizable in all proportions, but the products — like those obtained using preformed poly(ε-caprolactone) as the activator — are random block copolymers resulting from interchange reactions promoted by the base.[256,257] Similar partial randomizations occur in copolymerizations with methylcaprolactones and with laurolactam (azacyclotridecan-2-one).[258]

$$\text{O(CH}_2)_5\text{CO} \ + \ \text{:N(CH}_2)_5\text{CO} \longrightarrow \ ^-\text{O(CH}_2)_5\text{CON(CH}_2)_5\text{CO} \qquad (22)$$

$$(30) \hspace{5cm} (31)$$

Synthetic polypeptides (carbon-substituted nylon 2 polymers) are substances of considerable importance to the biophysicist as models of protein structure and function. They are usually prepared by the amine-initiated ring-opening polymerization of 4-substituted oxazolidin-2,5-diones which are the N-carboxyanhydrides (NCA) of α-aminocarboxylic acids, a reaction which proceeds with the concurrent elimination of carbon dioxide. By the use of amine-ended oligomers as initiators, block polymers containing polypeptide sequences can be obtained as shown in equation (23). Those with polystyryl or polydienyl segments are made using initiators of the types PCONHRNH$_2$ or P(CH$_2$)$_2$OCONHRNH$_2$ made by refunctionalization of carbochain oligomer anions as discussed earlier. If monofunctional they yield AB diblock polymers and, if bifunctional, ABA triblock polymers with a central carbochain unit.[127,128,259,260]

$$\text{P—NH}_2 \ + \ n \ \underset{\text{(NCA ring)}}{\square} \longrightarrow \text{P—NH[COCHRNH]}_n\text{H} \ + \ n\text{CO}_2 \qquad (23)$$

Since the polypeptide formed by the polymerization of an NCA with a simple amine is itself amine ended, sequential polymerizations can be conducted with different NCA monomers leading to AB diblock copolypeptides or, with a further cycle of operation using the original monomer, to ABA triblock copolymers. In the latter case, the outer A blocks may not be of equal lengths and, where such equality is required, a better procedure is to initiate the primary polymerization bidirectionally with a diamine according to the scheme of equation (24).[261-264]

By these various procedures block copolypeptides have been obtained with different combinations of crystalline, glassy or elastomeric, or hydrophilic and hydrophobic segments. In some cases, a sensitive group of the aminocarboxylic acid component has to be protected during the

$$H_2NRNH_2 + 2m \; [structure] \longrightarrow H[NHCHR^1CO]_n—NHRNH—[COCHR^1NH]_mH$$

$$\longrightarrow H[NHCHR^2CO]_n—[NHCHR^1CO]_m—NHRNH—[COCHR^1NH]_n—[COCHR^2NH]_mH \quad (24)$$

polymerization step and then released by post reaction; an example is the formation of polybutadiene-*block*-poly(L-lysine) shown in equation (25).[128]

$$PBdNH_2 + n \; [structure, (CH_2)_4NHCO_2CH_2Ph] \longrightarrow PBdNH[COCHNH]_nH \;|\; (CH_2)_4NHCO_2CH_2Ph$$

$$\xrightarrow{HCl/HBr} PBdNH[COCHNH]_nH \;|\; (CH_2)_4NH_2 \quad (25)$$

Interesting aspects of such block polymer syntheses are found in the use of a glycopeptide having a terminal asparagine residue to initiate the polymerization of γ-benzyl-L-glutamate NCA, yielding a polysaccharide–polypeptide block polymer,[265] and in the elegant demonstration that stereoselective blockiness is achievable in the first-named segments of poly(leucine)-*block*-poly(N^6-carbobenzoxy-DL-lysine) when DL-leucine NCA is polymerized with an optically active amine.[261]

Lastly, mention will be made of two further amide block copolymer syntheses not mentioned above. The first[266] employs living polymer anions from styrene, isoprene or methyl methacrylate to initiate the polymerization of isocyanates to diblock polymers containing nylon 1 sequences. In this approach, selective polymerization can be achieved at the unhindered isocyanate group of diisocyanates such as tolylene 2,4-diisocyanate to give products with pendant NCO groups (32) which are crosslinkable with diols to give tough resins.

$$R[—CH_2CH—]_n—[—CO—N—]_n \;|\; Ph$$

(32)

The second synthesis[267,268] commences with an acrylamido-ended prepolymer (33) which, by free radically initiated polymerization with styrene, gives bifurcated block products (34) of potential interest as novel non-thrombogenic biomedical materials.

$$H_2C=CHCO[N \; NCO(CH_2)_2N(CH_2)_2N(CH_2)_2CO]_n—N \; NCOCH=CH_2 \;|\; Me \;\; Me$$

(33)

$$\sim\sim P—N \; NCOCH \;|\; CH_2PS \;/\; PS$$

(34)

11.2.6 Polysiloxane Block Copolymers

Silicone polymers (polysiloxanes) form a group of materials of unusual properties which may include high-thermal stabilities, low-surface energies and low T_g values. Not surprisingly there has

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been long-standing interest in the incorporation of such components into block copolymer structures, and earlier work in this direction is reviewed in considerable detail in the two major monographs on block copolymers.[44,45] One particular group, the polysiloxane–poly(oxyalkylene) surfactants,[269-271] have already been mentioned as important aids in the manufacture of polyurethane foams, and much effor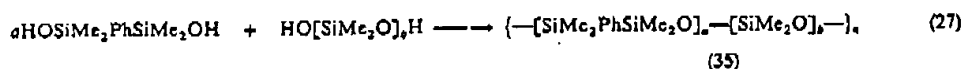t has been devoted to exploring the potentialities of other types of polysiloxane block polymers as elastomers and, more recently, as plastics materials. This section will review some methods of synthesis available in this field, noting first two factors which have to be taken into account in designing synthetic procedures and attainable molecular structures.

The first arises from the susceptibility of Si—O—Si linkages to undergo scission and bond re-formation by the action of strong bases (equations 26a and 26b). These processes can lead to a randomization ('shuffling' or equilibration) of siloxane units between polysiloxane chains and hence to a broadened distribution of MW's and often to the liberation of polysiloxane homopolymer, either during synthesis or on subsequent contact with bases. Care has therefore to be taken in the selection of basic initiators or catalysts for use in polymerization reactions in this series.

$$KOH + {-}{-}Si{-}O{-}Si{-} \rightleftharpoons {-}Si{-}O^-K^+ + HO{-}Si{-} \qquad (26a)$$

$$-Si{-}O^-K^+ + -Si{-}O{-}Si{-} \rightleftharpoons -Si{-}O{-}Si{-} + K^{+-}O{-}Si{-} \qquad (26b)$$
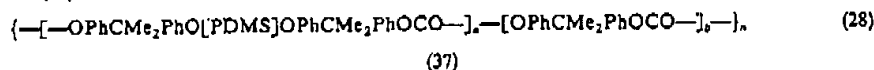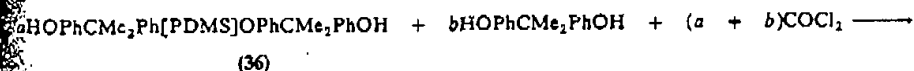
The second factor relates to the mode of attachment of polysiloxanyl units to the other components of structure in block copolymers; Si—O—C connections are relatively readily hydrolyzed and, in the interests of product stability, are better replaced where possible by more stable Si—C bonds.[272-275]
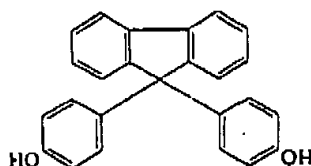
The principle of random block polymerization has been used for polysiloxane block copolymer synthesis as in equation (27) where the block connection is made by condensation between two types of silanol groups. This reaction, which is catalyzed by weak bases such as hexylamine carboxylate salts or tetramethylguanidine to avoid Si—O bond randomization, leads to multiblock polymers (35) having *p*-phenylene groups in the main chain.[61]

$$aHOSiMe_2PhSiMe_2OH + HO[SiMe_2O]_bH \longrightarrow \{-[SiMe_2PhSiMe_2O]_a{-}[SiMe_2O]_b{-}\}_x \qquad (27)$$

$$(35)$$

In other approaches, the polysiloxane [*e.g.* poly(dimethylsiloxane), poly(oxydimethylsilylene)] is furnished with functional organic end groups which are employed in subsequent conventional copolycondensation reactions. Thus polycarbonate–PDMS block polymers, which have been studied in considerable detail,[22,81,276-278] are obtained by end-capping α,ω-dichloro-PDMS with bisphenol A to give reactive oligomers (36) which are converted to block copolymers (37) by co-phosgenation with further quantities of the bisphenol (equation 28).

$$aHOPhCMe_2Ph[PDMS]OPhCMe_2PhOH + bHOPhCMe_2PhOH + (a + b)COCl_2 \longrightarrow$$

$$(36)$$

$$\{-[-OPhCMe_2PhO[PDMS]OPhCMe_2PhOCO{-}]_a{-}[OPhCMe_2PhOCO{-}]_b{-}\}_x \qquad (28)$$

$$(37)$$

The copolymers are clear tough materials with properties, depending on the *a:b* ratio, ranging from flexible elastomers to tough plastics. Use of the hindered bisphenol (38) in place of bisphenol A gives rise to transparent thermoplasts of exceptionally high T_g and possessing an impressive level of fire-safety performance.[279-281]

$$(38)$$

392

Heterochain Block Copolymers

Table 5　Polysiloxane Block Polymers by Oligomer Combination Reactions

Polysiloxane Oligomer	Additional Oligomers and Other Reactant(s)	Product Type	Ref.
ClCO-m-PhCO₂[PDMS]O₂C-m-PhCOCl	H[HN-m-PhNHCO-m-PhCO]ₙNH-m-PhNH₂	PDMS-block-polyamide	80
⁻O₄Cl⁺SiMe₂[PDMS]SiMe₂⁺ClO₄⁻	-PS-	PDMS-block-polystyrene	156
Cl[PDMS]SiMe₂Cl	HOSiMe₂PSSiMe₂OH/pyridine	PDMS-block-polystyrene	282
Cl[PDMS]SiMe₂Cl	HO(CH₂)₆O[CO(CH₂)₈CO₂(CH₂)₆O]ₙH/pyridine	PDMS-block-polyester	283, 284
Cl[PDMS]SiMe₂Cl	Hydroxyl-ended poly(ethylene adipate-co-maleate)/ N-methylmorpholine	PDMS-block-unsaturated copolyester	285
HO[PDMS]SiMe₂OH	HO[CH₂CH₂]ₙOH/tin(II) octoate	PDMS-block-polyethylene	286

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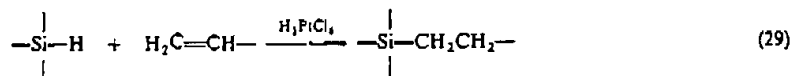dialkylam
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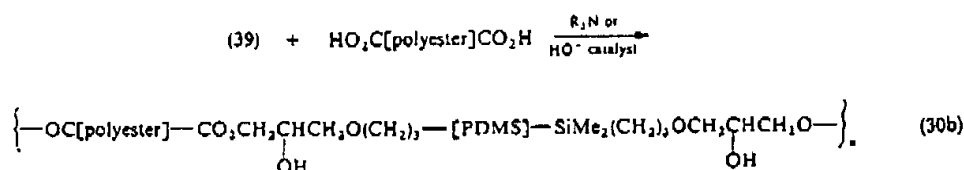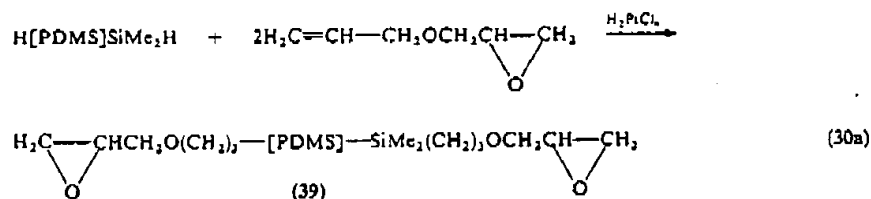PDMS w
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In an analogous synthesis α,ω-di(m-aminophenyl)PDMS oligomers have been condensed with m-phenylenediamine and isophthaloyl chloride to give poly(m-phenyleneisophthalamide)–PDMS block copolymers.[60]

The next class of reactions to be considered is that yielding polysiloxane block or segmented polymers by oligomer combination. Some simple examples are given in Table 5. These have been supplemented by two types of reactions that are specific to organosilicon chemistry.
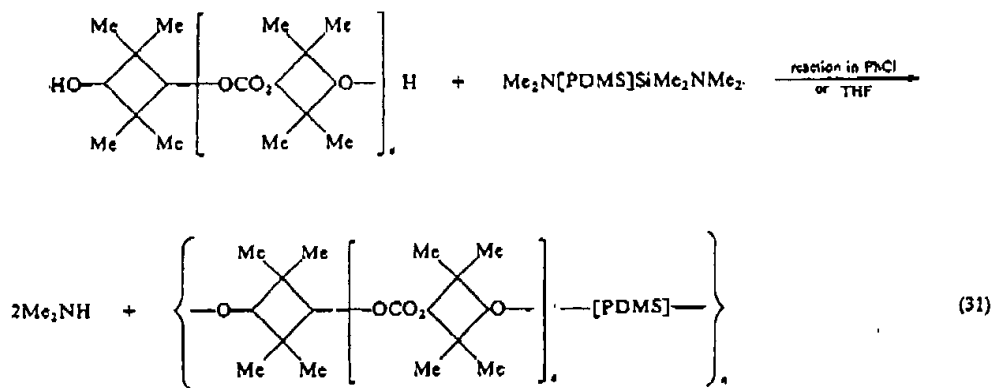
The first comprises the reaction of addition which occurs between hydridosilane and vinyl groups, usually catalyzed by chloroplatinic acid, forming Si—C bonds (equation 29).
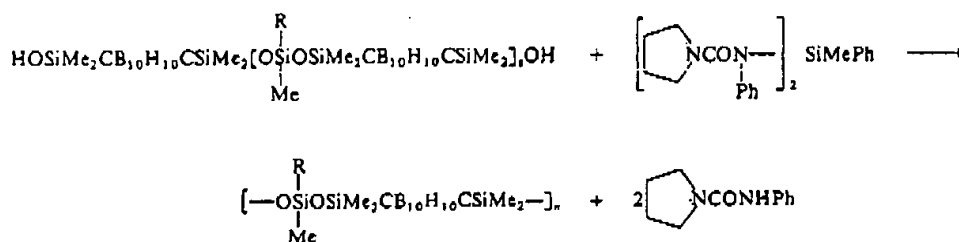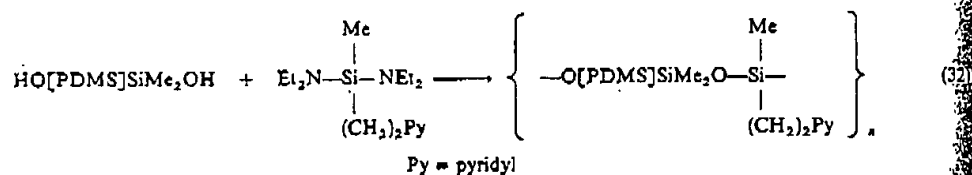
$$\overset{|}{\underset{|}{-Si}}-H \; + \; H_2C{=}CH{-} \; \xrightarrow{H_2PtCl_6} \; \overset{|}{\underset{|}{-Si}}-CH_2CH_2{-} \tag{29}$$

The reaction can be adapted to block polymer formation in various ways, *e.g.* by forming polystyrenes with —SiMe$_2$CH=CH$_2$ or —CH$_2$SiMe$_2$CH=CH$_2$ end groups and combining these with mono- or di-hydrido-ended PDMS oligomers, or inversely by reacting α,ω-di(hydridodimethylsilyl)polystyrenes with PDMS oligomers having allyloxy end groups.[275,282,287] Another variant uses the hydrosilylation reaction to attach epoxide end groups to the ends of a PDMS chain, giving oligomers (39) which can form block copolymers by ring-opening polyaddition to carboxyl-ended polyesters (equations 30a and 30b).[274]

$$H[PDMS]SiMe_2H \; + \; 2H_2C{=}CH{-}CH_2OCH_2CH{-}CH_2 \; \xrightarrow{H_2PtCl_6}$$

$$H_2C{-}CHCH_2O(CH_2)_3{-}[PDMS]{-}SiMe_2(CH_2)_3OCH_2CH{-}CH_2 \tag{30a}$$

$$(39)$$

$$(39) \; + \; HO_2C[polyester]CO_2H \; \xrightarrow[HO^- \text{ catalyst}]{R_3N \text{ or}}$$

$$\left\{ {-}OC[polyester]{-}CO_2CH_2\underset{OH}{CH}CH_2O(CH_2)_3{-}[PDMS]{-}SiMe_2(CH_2)_3OCH_2\underset{OH}{CH}CH_2O{-} \right\}_n \tag{30b}$$

The second specific reaction is that of condensation between polysiloxane oligomers with dialkylamino end groups and hydroxyl-ended co-reactant oligomers; dialkylamine is eliminated as Si—O bonds are formed. The OH groups of the co-reactants may be phenolic or alcoholic, the former being the more reactive. The approach has been used to obtain multiblock polymers of PDMS with a variety of other species;[264,290] an example leading to a polyester-*block*-polysiloxane product is shown in equation (31), and one using silanol end groups in equation (32).[289] Ultrahigh MW segmented poly(carboranesiloxane) polymers have also been obtained by the coupling reaction shown in equation (33).[290]

$$HO{-}\langle\rangle{-}OCO_2{-}\langle\rangle{-}O{-}]_4 H \; + \; Me_2N[PDMS]SiMe_2NMe_2 \; \xrightarrow[\text{or THF}]{\text{reaction in PhCl}}$$

$$2Me_2NH \; + \; \left\{ {-}O{-}\langle\rangle{-}OCO_2{-}\langle\rangle{-}O{-}]_4 {-}[PDMS]{-} \right\}_4 \tag{31}$$

394　　　　　　　　　　　　　　*Heterochain Block Copolymers*

$$HO[PDMS]SiMe_2OH \ + \ Et_2N{-}\overset{\overset{Me}{|}}{\underset{\underset{(CH_2)_2Py}{|}}{Si}}{-}NEt_2 \ \longrightarrow \ \left\{ {-}O[PDMS]SiMe_2O{-}\overset{\overset{Me}{|}}{\underset{\underset{(CH_2)_2Py}{|}}{Si}}{-} \right\}_n \tag{32}$$

Py = pyridyl

$$HOSiMe_2CB_{10}H_{10}CSiMe_2[O\overset{\overset{R}{|}}{\underset{\underset{Me}{|}}{Si}}OSiMe_2CB_{10}H_{10}CSiMe_2]_xOH \ + \ \left[\left\langle \!\!\! \bigcirc \!\!\! \right\rangle NCON{-}\underset{Ph}{|} \right]_2 SiMePh \ \longrightarrow$$

$$[{-}O\overset{\overset{R}{|}}{\underset{\underset{Me}{|}}{Si}}OSiMe_2CB_{10}H_{10}CSiMe_2{-}]_n \ + \ 2 \left\langle \!\!\! \bigcirc \!\!\! \right\rangle NCONHPh \tag{33}$$
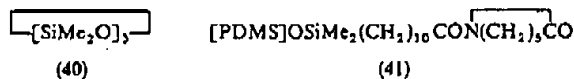
As with other classes of polymers considered above, ring-opening polymerization has also been employed as the basis of another general approach to the synthesis of siloxane block copolymers, in this case by the anionic polymerization of cyclopolysiloxanes in ways which yield either polysiloxane-*block*-polysiloxane products or those containing polysiloxane and other structural classes of blocks.

The proneness of siloxane bonds to undergo cleavage in strongly basic conditions imposes the need for a specific choice of polymerizable cyclopolysiloxane and of the initiator counterion if well defined products are to result. The most readily available monomer, octamethylcyclotetrasiloxane, is particularly susceptible to bond randomization, leading to the problems already mentioned. However, these can be avoided by use of the cyclic trimer hexamethylcyclotrisiloxane (40). Through its greater reactivity, this substance is open to polymerization by weaker bases such as lithium silanolates or the lithium salts of hydrocarbon polymer anions which do not promote the equilibrium reaction. By initiating the polymerization of (40) with MePh$_2$SiOLi or LiOSiPh$_2$OLi and reacting the resultant LiOSiMe$_2$-ended polymer with hexaphenylcyclotrisiloxane, polymers of [SiMe$_2$O]$_a$-*block*-[SiPh$_2$O]$_b$ structure have been formed.[62] Correspondingly, initiation with PS$^-$Li$^+$, Li$^+$ $^-$PS$^-$Li$^+$ or analogous polydienyl species gives rise to PS-PDMS, PDMS-PS-PDMS and polydiene–PDMS block copolymers.[63,125,291-294] Silanolate end groups are not themselves sufficiently nucleophilic to initiate the polymerization of vinyl monomers, and the approach cannot therefore be extended to the direct synthesis of ABA copolymers with PDMS units as the central segments. To obtain such materials, recourse must be made to the coupling of silanol- or silanolate-ended diblock polymers by reagents such as Me$_2$SiCl$_2$ or Ph$_2$Si(OAc)$_2$;[295,296] multiblock polysiloxane copolymers have been made by the similar reactions of BAB copolymers having outer siloxane blocks.[125]

Lastly, reference may be made to the use of the *N*-acyllactam-ended oligomer (41), itself prepared with the aid of several of the reactions already discussed, as an activator for the anionic polymerization of ε-caprolactam, yielding PDMS–nylon 6 block copolymers.[297]

$$\underset{(40)}{\underline{[SiMe_2O]_3}} \qquad\qquad \underset{(41)}{[PDMS]OSiMe_2(CH_2)_{10}CON(CH_2)_5CO}$$

11.2.7 Polysulfone Block Copolymers

The strong dipoles of sulfone $-(SO_2)-$ groups incorporated as recurring features of structure in polymer chains exercise a powerful elevating effect on intermolecular cohesion, comparable with that conferred by the CONH groups in polyamides. Of the many known types of polymer containing sulfone groups, particular interest attaches to the poly(arylene sulfones) and poly(arylene ether sulfones) which were discovered in the 1960s and are now well established as high-performance engineering thermoplasts.[206] Investigation in this field has recently been extended to block copolymers, particularly of poly[oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene (1-methylethylidene)-1,4-phenylene] (42) which, for ease of presentation, will be the only polysulfone considered in this section. The polymer is prepared by the polyetherification of bisphenol A with 4,4'-dichlorodiphenyl sulfone in the presence of a base. By control of the reactant stoichiometry, it
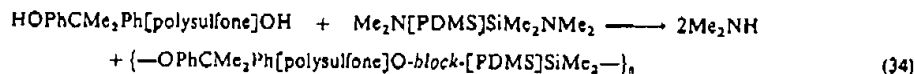
oligomers can be obtained either with phenolic or with *p*-chlorophenylsulfonyl groups at both ends of the molecule; both forms have been employed in the synthesis of block copolymers.
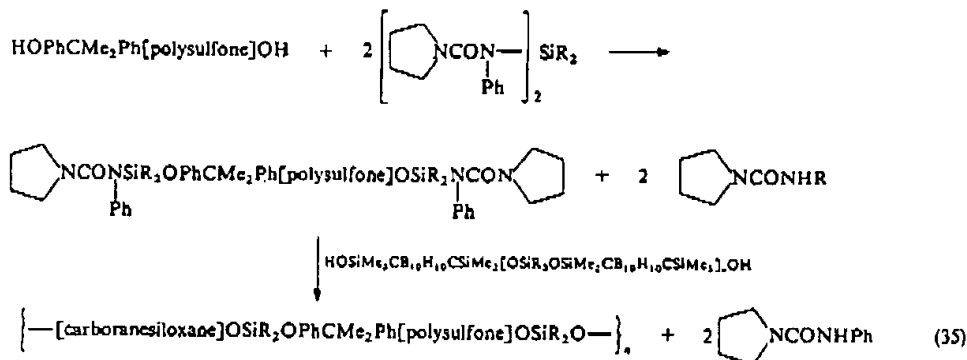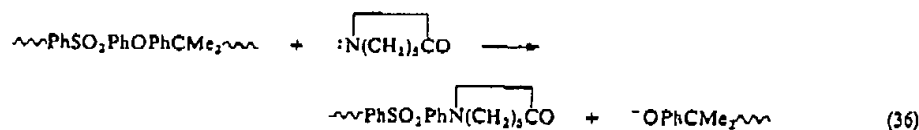
$$[-OPhSO_2PhOPhCMe_2Ph-]_n$$

(42)

The formation of polysulfone-*block*-PDMS block copolymers has thus been accomplished by use of the silylamine–OH reaction as shown in equation (34). The products are transparent materials with properties ranging from elastomeric to rigid thermoplastic as the polysulfone content increases.[24,288,298]

$$HOPhCMe_2Ph[polysulfone]OH \ + \ Me_2N[PDMS]SiMe_2NMe_2 \longrightarrow 2Me_2NH$$

$$+ \{-OPhCMe_2Ph[polysulfone]O\text{-}block\text{-}[PDMS]SiMe_2-\}_n$$

(34)

Polysulfone–BPAC block copolymers have been prepared by three types of reactions which lead to products having different degrees of structural order: (a) by the random block copolymerization of hydroxyl-ended polysulfone oligomers with bisphenol A and phosgene;[299,300] (b) by the cophosgenation of mixtures of hydroxyl-ended polysulfone and BPAC oligomers;[301] and (c) by the condensation of hydroxyl-ended polysulfone with α,ω-chloroformate-ended BPAC oligomers.[300,302] From the nature of both constituent units, these block copolymers are tough thermoplasts, those with polysulfone blocks of MW < 16 000 being homogeneous single-phase materials. Polysulfone block copolymers with polystyrene or with 4G.T sequences have been prepared by similar reactions. Polysulfone–poly(carboranesiloxane) block polymers have also been obtained by a sequence of reactions commencing with hydroxyl-ended polysulfone oligomers (equation 35); these materials possess high resistance towards thermal oxidation.[303]
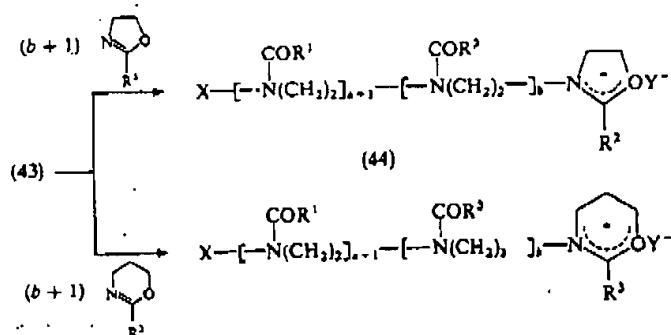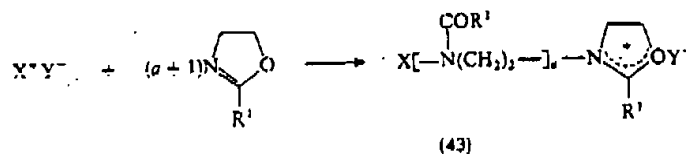

Polysulfone–nylon 6 block copolymers have been obtained by utilizing the interesting ability of *p*-chlorophenylsulfonyl-ended polysulfone oligomers to serve as activators for the anionic polymerization of ε-caprolactam. The activation depends on the formation of N-(*p*-phenylenesulfonyl-*p*-phenylene)-ε-caprolactam end groups, and these can also be formed by means of an alternative and simpler procedure involving the addition of sodium hydride to molten polysulfone–lactam mixtures when ether groups of the polysulfone chain are cleaved by the lactamate anions generated *in situ* (equation 36); the reaction has a formal resemblance to the poly(caprolactone)–lactam copolymerization mentioned earlier. The polysulfone–nylon 6 copolymers are two-phase materials which are compatible with both of the related homopolymers and display some advantages of mechanical properties over those of polysulfone resins.[304,305]
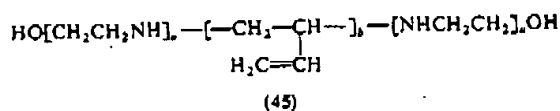

11.2.8 Other Block Copolymers

Some further approaches to the synthesis of heterochain block copolymers, not included in earlier sections, are summarized below.
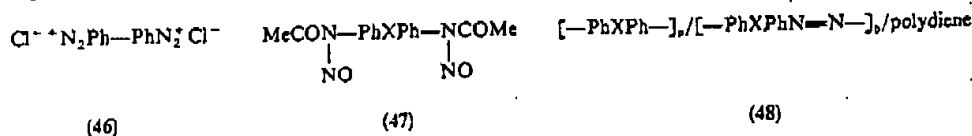
(a) Under initiation by ionic or ionogenic substances such as protic acids, oxazolinium salts, alkyl iodides or alkyl *p*-toluenesulfonates, 2-oxazolines undergo living polymerization to products with oxazolinium end groups (43) (equation 37). These can initiate the polymerization of a second oxazoline or of an oxazine monomer in a sequential manner to give block copolymers composed of different types of poly(*N*-acylaziridine) segments as shown in equation (38).[306,307] Polymers of the structure (44) with R^1 = undecyl and R^2 = ethyl represent combinations of hydrophobic and hydrophilic blocks and are surfactants.
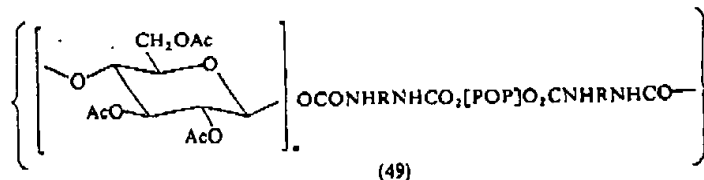

(43)

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An alternative synthesis of block copolymers based on 2-oxazolines employs oligomeric initiator cations or procations, as in the polymerizaton of 2-methyl-2-oxazoline with iodo-ended poly(phenyloxirane),[308] and in that of 2-oxazoline with the di-*p*-toluenesulfonate of α,ω-di(2-hydroxyethyl)-1,2-polybutadiene; the last-mentioned reaction gives rise to poly(*N*-formylaziridine)-*block*-polybutadiene-*block*-poly(*N*-formylaziridine) which can be converted, by removal of its formyl groups, to the block copolyamine (45).[137]

$$HO[CH_2CH_2NH]_a-[-CH_2-CH-]_b-[NHCH_2CH_2]_cOH$$
$$H_2C=CH$$

(45)

(b) The decompositions of the bis(diazonium chloride) (46) and of bis(*N*-nitroso-*N*-acetylamine) (47) in the presence of dienes have been studied in attempts to obtain flexible electronically conducting polymers which might be miscible with (and hence dispersible in) non-conducting organic polymers.[309,310] The ensuing reactions of radical formation and recombination give rise to block polymers of imperfect structure containing the structural units shown in (48).

$$Cl^-{}^+N_2Ph-PhN_2^+\,Cl^-$$

$$MeCON-PhXPh-NCOMe$$
$$NO\qquad\qquad NO$$

$$[-PhXPh-]_a/[-PhXPhN=N-]_b/polydiene$$

(46)　　　　　　　　　　(47)　　　　　　　　　　(48)

(c) Polymers containing cellulose or amylose blocks have been prepared by the controlled hydrolysis of the polysaccharide triacetates to hydroxyl-ended triacetate oligomers of controlled chain lengths. By coupling with diisocyanate end-capped poly(oxypropylene) or polybutadiene diols these were converted to products of the type exemplified in (49) and thence, by methanolysis of the

(49)

acetate groups, to polysaccharide–polyether or polysaccharide–polybutadiene multiblock copolymers some of which have interest as biodegradable film-forming materials.[35,38,40]

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